

THE ROLE OF WETLAND SOILS IN NITROGEN AND PHOSPHORUS REMOVAL  
FROM AGRICULTURAL DRAINAGE WATER

By

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In recent years, much attention has been focused on nutrient losses in drainage water from agricultural lands. One of the approaches to nutrient removal from agricultural drainage water is the use of wetland retention/detention areas. A series of laboratory studies was conducted to evaluate the role of wetland soils in nitrogen and phosphorus removal from agricultural drainage water.

The extent of denitrification in soil in the absence of overlying water was determined to evaluate denitrification potential of the soils. At least 96% of added  $^{15}\text{N}$ -labeled nitrate was lost rapidly from the soil within a 2 to 6 day period. Nitrification and denitrification in simulated wetland systems were investigated by adding  $^{15}\text{N}$ -labeled ammonium or  $^{15}\text{N}$ -labeled nitrate to the overlying water of the soil-water columns. After 25 days, 43 to 84% of the added ammonium was removed from the overlying water. Ammonium removal rate was apparently influenced by soil characteristics, especially soil pH. Estimated ammonium removal in soil-water systems ranged from 0.31 to 0.63  $\mu\text{g N/ml/day}$ . Denitrification in soil-water systems appeared to follow first-order

kinetics with the rate constants ranging from 0.02 to 0.062 day<sup>-1</sup>. Nitrate removal rate increased with soil organic matter content and soil pH.

Phosphorus adsorption maxima ranged from 62 to 2,030 µg P/g soil indicating that wetland soils have high phosphorus removal potential. For all soils except two, phosphorus sorption decreased under anaerobic conditions; however, considerable amounts of phosphorus were retained by most soils under either aerobic or anaerobic conditions. In laboratory column studies, underlying soil readily adsorbed phosphorus from the overlying water. Approximately 54 to 88% of the initial phosphorus in the overlying water was removed in 25 days.

The extent of nutrient release from decomposing plant material was evaluated in simulated wetland systems. The rate of plant decomposition in these systems decreased with decreasing pH. Aeration did not have measurable effect on rate of plant decomposition. Underlying soils, in two of three cases, retained most of the nitrogen and phosphorus released during the plant decomposition process.

## CHAPTER I

### INTRODUCTION

Nutrient losses in drainage water from agricultural lands have received much attention in recent years. The addition of nutrients, especially nitrogen and phosphorus, from agricultural drainage water is one of the potential causes of pollution of lakes and streams. Use of either natural or manmade wetland retention/detention areas is a proposed approach to nutrient removal from sewage effluent and from agricultural drainage water (Sprangler et al., 1976; Fritz and Helle, 1978; Blumer, 1978; Tilton and Kadlec, 1979; Boyt et al., 1977). Nutrient removal can be partially accomplished by plant uptake. Also, the chemistry and biochemistry of nitrogen and phosphorus in wetland systems are such that hydrosol can act as an important sink for these nutrients.

Nitrogen is present in both organic and inorganic forms in agricultural drainage water. The organic nitrogen undergoes ammonification to form inorganic nitrogen, namely ammonium which can be further transformed to nitrate through nitrification. Inorganic nitrogen, ammonia and nitrate, may be removed as a result of ammonia volatilization and/or denitrification reactions depending on physico-chemical characteristics of the soil-water system (Engler and Patrick, 1974; Patrick and Reddy, 1976; Reddy et al., 1976; Vlek and Craswell, 1979). Due to the existence of an aerobic zone (overlying water and aerobic soil layer) and an anaerobic zone (anaerobic soil layer) in wetland systems,

nitrification-denitrification reactions are generally found to be the major mechanisms for nitrogen removal in these systems. Ammonia volatilization becomes a less favorable pathway for the loss of nitrogen because of the low pH common to most wetland systems.

Phosphorus in agricultural drainage water is also present in both organic and inorganic forms. Little information is available on the forms and amounts of organic phosphorus in drainage water. Inorganic phosphorus generally predominates and occurs as the orthophosphate anion ( $\text{PO}_4^{-3}$ ) which may exist in forms of  $\text{H}_2\text{PO}_4^{-}$  and  $\text{HPO}_4^{-2}$ . Orthophosphorus is removed mainly by sorption to the underlying sediments. The capacity of sediment to sorb phosphorus depends on the concentration of phosphorus in solution, pH, and adsorption characteristics of the sediments.

The overall objective of this study was to evaluate the effectiveness of soil in wetland retention/detention areas for removing nutrients from agricultural drainage water. To accomplish this, a series of laboratory experiments was conducted to evaluate

- a) nitrogen removal potential due to nitrification/denitrification,
- b) capacity of wetland soils to fix and retain phosphorus under redox conditions found in wetland systems,
- c) nutrient availability from plant materials decaying at the soil surface.

This study was part of a broader study on the use of natural and recreated wetlands, so called retention/detention areas, to filter agricultural runoff from the Kissimmee River Valley and Taylor Creek-Nubbin Slough Basin proposed by the coordinating Council on the Restoration of the Kissimmee River Valley and Taylor Creek-Nubbin Slough Basin.

## CHAPTER II

### LITERATURE REVIEW

#### I. Nitrogen Removal from Agricultural Drainage Water by Wetland Soils

##### A. Forms and Sources of Nitrogen

Nitrogen in soils, sediments, and overlying water occurs predominantly as complex organic substances with only small amounts present as inorganic nitrogen. Organic nitrogen consists primarily of amino acids and amines (proteinaceous nitrogen), along with some heterocyclic compounds such as purines and pyrimidines (Brezonik, 1972), and humic compounds with low nitrogen content. Inorganic nitrogen consists of ammonia, ammonium, nitrite, nitrate, and molecular nitrogen. Ammonium is mainly derived from organic nitrogen via the ammonification process and is present predominantly in reduced environments such as sediments. The gaseous forms of nitrogen, ammonia and molecular nitrogen, are produced under reduced conditions, especially in sediments and flooded soils. Both nitrite and nitrate occur in very small amounts in sediments, while nitrate is present in larger amounts in overlying water.

Sources of nitrogen in wetlands are (1) nitrogen mineralization from soil organic matter and plant residues; (2) nitrogen fixation in the water and sediment; (3) precipitation on the surface soil and sediment; and (4) other external sources such as waste water effluent and drainage water from agricultural lands.



Significant amounts of nitrogen may be lost from agricultural lands in drainage water (Miller, 1955; Vollenweider, 1968; Hutchinson and Viets, 1969; Messer and Brezonik, 1977; Kudeyarov and Bashkin, 1980; Baker and Johnson, 1981; Fellows and Brezonik, 1981). It has been estimated that pastured areas contributed approximately 1 to 8.5 kg N/ha/yr to lakes (Miller, 1955; Vollenweider, 1968). Nitrogen input from agricultural backpumping into Lake Okeechobee which is surrounded by a variety of agricultural areas, was estimated by Davis and Marshall (1975) to be about  $5.86 \times 10^9$  g/yr. Kudeyarov and Bashkin (1980) found that fertilizer from agricultural and forestry areas along the Skniga river basin in Russia contributed about 77.3% of the total nitrogen input (2,121 tons) in their 1977 nitrogen balance in this small river basin. Reddy and Graetz (1981) observed large quantities of nitrogen released from organic soils planted to vegetable crops located in Zellwood, Florida, as indicated by the concentration of total nitrogen ( $7.2 \mu\text{g N/ml}$ ) in the drainage canal water. According to Fellows and Brezonik (1981), approximately 270 kg of N seeped into the West Pool (a section of Lake Conway, Florida) from a 4.8 ha of excessively fertilized citrus grove with 900 kg N/ha. This was equivalent to  $0.14 \text{ g N/m}^2$  ( $1.4 \text{ kg N/ha}$ ) of lake surface over the 229-day period. Nitrogen contributed to the lake from a regularly fertilized grove was the same as background levels. Nitrogen from agricultural areas can also be transported by air to lakes and streams. Hutchinson and Viets (1969) found that significant amounts of ammonia were contributed to the nitrogen budgets of downwind lakes by ammonia volatilization from cattle feedlots.

## B. Nitrogen Transformations in Flooded Soil Systems

Forms of nitrogen in soil-water systems can be changed through a series of biochemical and physico-chemical processes. Organic nitrogen can be converted to ammonium through the ammonification process. Under aerobic conditions ammonium can further be converted to nitrate via the nitrification process. Nitrogen species in gaseous forms, namely ammonia and  $N_2$ , can be released from the soil-water system to the atmosphere by ammonia volatilization and denitrification, respectively. These processes will be discussed in more detail in the following section. The nitrogen cycle, in general, traces the flow of nitrogen from inorganic forms into living systems and then back again into inorganic forms. Although the nitrogen cycle of flooded soils is understood qualitatively in appreciable detail, quantitative rates of transformations are delineated less clearly, especially at the soil-water interface.

Major biological, chemical, and physical nitrogen transformations in flooded soils is illustrated in Figure 1. The processes involved in the loss of nitrogen from flooded soils are ammonia volatilization and nitrification-denitrification. Due to increasing concerns over efficiency of nitrogen fertilizer used in growing lowland rice and also increasing use of wetland area in removal of nitrogen from waste water, these processes in flooded soils and sediments have recently been examined more closely.

The occurrence and rates of each process in flooded soils are quite different from those in well-drained soils. Differences can mainly be attributed to the small amounts of oxygen or lack of oxygen in

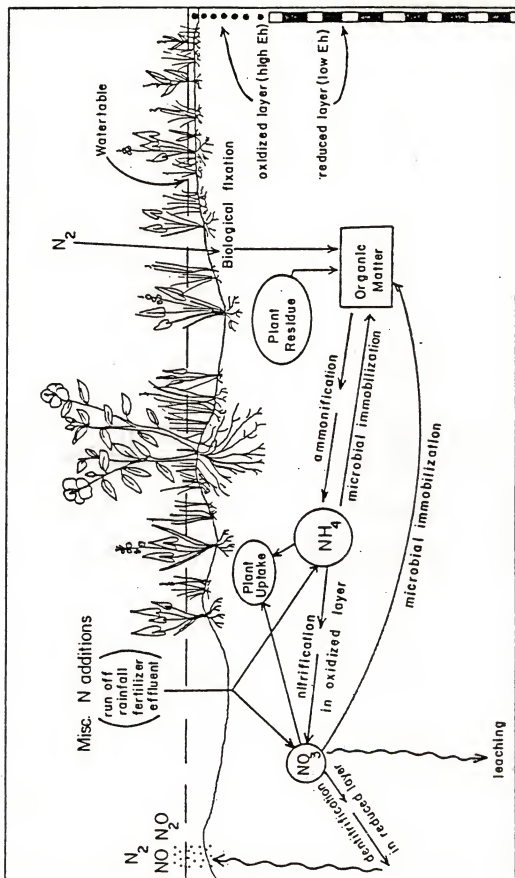


Figure 1. Nitrogen transformations in flooded soils.

flooded soil systems. Generally flooded soils are characterized by the absence of molecular oxygen throughout most of the soil profile. Oxygen movement through the overlying water is usually much slower than the rate at which oxygen can be reduced in the soil (Patrick and Mahapatra, 1968; Howeler and Bouldin, 1971; Patrick and Delaune, 1972). The high rate of oxygen depletion in flooded soil is due to the uptake of oxygen by microorganisms, plant roots, and animal respiration. Due to the high consumption of oxygen in the soils, two layers, namely oxidized or aerobic, and reduced or anaerobic, are formed in flooded soils (Figure 2). In the aerobic layer oxygen is supplied from the overlying water. Atmospheric oxygen can also be supplied to the aerobic layer by rice and other swamp and marsh plants which transport oxygen through the stem and roots, and some of this oxygen diffuses from the root into the adjacent soil layer. The thickness of the aerobic layer is determined by the net effects of the oxygen consumption rate in the soil and the oxygen supply rate through the flood water. Several workers (Armstrong and Boatman, 1967; Yunkervich et al., 1966; Pamatat and Banse, 1969) observed that flooded soils and lake and ocean muds are anaerobic. Ponnampertuma (1972) compared the rate of oxygen consumption by lake and ocean mud ( $2 \times 10^{10}$  to  $2 \times 10^9$  g/cm<sup>2</sup>/sec) given by Hutchinson (1957), Pamatat and Banse (1969) with oxygen diffusion rates in saturated soils ( $1 \times 10^{12}$  g/cm<sup>2</sup>/sec) estimated by Howeler and Bouldin (1971) and concluded that flooded soils and lake and ocean muds should be anaerobic below the soil-water interface.

Because of the lack of oxygen in flooded soils, the mineralization of organic nitrogen stops at ammonium. Therefore, ammonium accumulation can be found in anaerobic soils and anoxic water. However, the

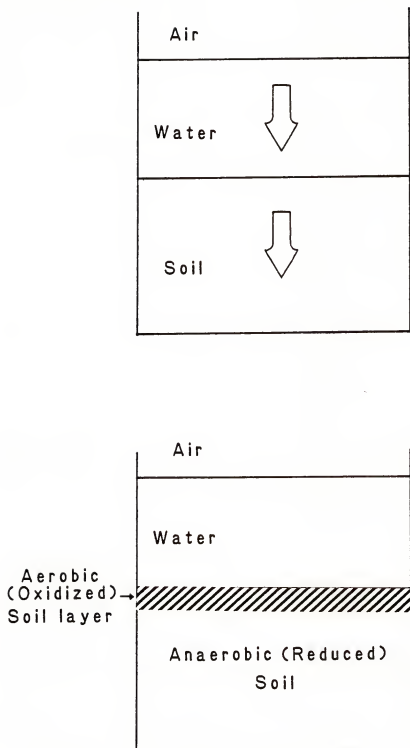


Figure 2. Development of aerobic (oxidized) soil layer.  
(Patrick and Mahapatra, 1968).

formation of aerobic and anaerobic layers favors simultaneous nitrification and denitrification reactions in flooded soils or sediments.

Nitrification, oxidation of ammonium to nitrate, occurs in the surface aerobic layer and denitrification, reduction of nitrate to  $N_2$  and  $N_2O$ , occurs in the subsurface anaerobic layer. Therefore, nitrification-denitrification is one of the major reactions responsible for nitrogen removal from flooded or wetland soils.

1. Ammonification. Ammonification is the first step in mineralization of organic nitrogen (Alexander, 1977). Ammonification is the microbial conversion of organic nitrogen to inorganic nitrogen as ammonium. This process is considered to be the rate limiting step in mineralization of soil organic nitrogen, and over much of the temperature range of 0 to 35°C, almost complete conversion of ammonium to nitrate normally occurs in aerated soils (Stanford et al., 1973). However, mineralization of organic nitrogen stops at ammonium in flooded soils because of the absence of oxygen which is required for microbial conversion of ammonium to nitrate. Therefore, ammonium generally accumulates in the anaerobic zone of the flooded soil system. Despite slow rates of ammonification and nitrification found in flooded soil (Stanford et al., 1972, 1973; Alexander, 1977), net mineralization in flooded soils is generally greater than in well-drained soils because of the low nitrogen requirement of anaerobic microorganisms (Tusneem and Patrick, 1971; Waring and Bremner, 1964).

2. Ammonia volatilization. Ammonia volatilization can be considered as an important mechanism of nitrogen loss from flooded soil only when high ammonia concentrations coexist with high pH, high

temperature, and low cation-exchange capacity. Losses of nitrogen via ammonia volatilization from flooded soils are often insignificant when pH is below 8.0. Ventura and Yoshida (1977) found that below pH 7.5, a very small amount of ammonium fertilizer was lost by ammonia volatilization but increased greatly with increases in soil pH. Extent of ammonia loss from soil-water systems by volatilization depends on the distribution of ammonia in the soil-water profile. Less ammonia loss would be expected if the major portion of ammonia is in the deep sediments rather than in the sediment surface or overlying water. As shown by Ernst and Massey (1960) and MacRae and Ancajas (1970), losses of ammonia are greater when ammonium fertilizer is broadcast to the surface of a wet soil than when it is incorporated into the soil.

Rate of ammonia volatilization from a water surface can be affected by the ammonium concentration in solution, temperature, wind velocity at the surface of the water and water turbulence (Stratton, 1968; Fenn and Kissel, 1976; Vlek and Stumpe, 1978). The carbon dioxide balance between photosynthesis and respiration can also affect the rate of ammonia volatilization. During the day, carbon dioxide can be depleted due to photosynthesis by algae and aquatic plants resulting in high water pH which can increase the rate of ammonia volatilization (Bouldin and Alimagno, 1976).

3. Nitrification. Nitrification involves the biological conversion of inorganic nitrogen from a reduced to a more oxidized state. Under this broad definition are included autotrophic and heterotrophic nitrification. Except for certain photochemically induced reactions that form nitrate from nitrogen oxides in the atmosphere, biological nitrification is the only natural source of nitrate in the biosphere.

Nitrification is important in soils, natural waters, and sewage systems and has been reviewed by Alexander (1965), Keeney (1973), Verstraete and Alexander (1973), Focht and Chang (1975), and Focht and Verstraete (1977).

Autotrophic nitrification is a two-step process, with both steps mediated primarily by obligate aerobic bacteria. The autotrophic nitrification sequence involves a conversion of nitrogen from  $-3(\text{NH}_3)$  to  $+5(\text{NO}_3)$  oxidation state, a span involving the release of 8 electrons (Alexander, 1965). The bacteria responsible for the process are chemoautotrophic organisms that obtain their energy by oxidizing reduced forms of nitrogen, and obtain their carbon from carbon dioxide. The most commonly mentioned nitrifying bacteria involved in the first step, which produces nitrite from ammonia, are in the genus Nitrosomonas. The second step in nitrification is the oxidation of nitrite to nitrate. The nitrifiers which are responsible for this step are primarily of the genus Nitrobacter. Nitrite usually does not accumulate during nitrification, except in high pH and/or low temperature conditions that are more unfavorable to Nitrobacter than to Nitrosomonas.

A second type of nitrification that has been studied only in recent years is heterotrophic nitrification. A variety of heterotrophic bacteria, fungi, and actinomycetes can oxidize reduced species of nitrogen to form a variety of products (Eylar and Schmidt, 1959; Hirsch et al., 1961; Verstraete and Alexander, 1973; Tate, 1977). The heterotrophic nitrifier Arthrobacter is reported to excrete hydroxylamine, a hydroxamic acid, nitrite, nitrate, and a compound tentatively identified as 1-nitrosoethanol (Verstraete and Alexander, 1972). Tate (1977) also observed that Arthrobacter is responsible for the production



of nitrite and/or nitrate from reduced nitrogenous compounds in histosols which contain insufficient populations of Nitrosomonas and Nitrobacter. Heterotrophic nitrification may account for some of the nitrogen oxidized in nature, though probably its contribution is very small. However, under appropriate conditions of pH, carbon availability, and nitrogen supply, heterotrophic nitrification may take place and give rise to the formation of inorganic and organic nitrogenous products. Some of these compounds, such as hydroxylamine, nitrite, and l-nitrosoethanol, may be a hazard to man and animals.

Studies on nitrification in lake systems have been done by several researchers (Brezonik, 1968; Chen et al., 1972; Isirimah et al., 1976; Graetz et al., 1973; Sompongse, 1978; Vincent and Downes, 1981). Brezonik (1968) measured nitrification rates in Lake Mendota using a  $^{15}\text{N}$  technique, and found that substantial nitrification occurred at mid-depth (7 to 17 m) in this lake during late spring and early summer. Similar nitrification rates were observed in the water column of Lake Conway during the fall overturn (Sompongse, 1978). They also emphasized that this nitrate production increased the importance of denitrification as a nitrogen sink in lakes. Nitrification was also observed in the water column of Blelham Tarn, English Lake District, during stratification with the highest nitrification rate in the upper hypolimnion, where numbers of autotrophic nitrifiers were highest (Christofi et al., 1981). According to Billen (1975), nitrification occurred in the overlying water rather than the sediment of the estuary. Laboratory studies by Graetz et al. (1973) indicated that nitrification in freshwater lakes occurred at a rapid rate when the overlying water was aerated. Several

researchers found that nitrification can also occur readily in aerobic sediments (Chen et al., 1972; Isirimah et al., 1976; Curtis et al., 1975; Vincent and Downes, 1981; Henriksen et al., 1981). Chen and his colleagues have shown that nitrification proceeds readily in lake sediments if they are stirred vigorously to provide oxygen. They also found that most, if not all, nitrification in these sediments was mediated by autotrophs. In a study of nitrogen cycling in Lake Wingra, Isirimah et al. (1976) found a relatively slow nitrification rate in the water column which they attributed to heterotrophic organisms. However, they found rapid autotrophic nitrification in the sediments. Vincent and Downes (1981) reported that deep water accumulation of nitrate in Lake Taupo was due to benthic rather than planktonic nitrification. This was illustrated by the fast rate of benthic nitrification in the top 2.5 mm of sediments and also the least active nitrifying bacteria in the deep hypolimnion.

The rate of nitrification has been shown to depend on aeration and pH. Oxygen is an obligate requirement for all species of nitrifiers. If the oxygen supply is inadequate for microorganisms, there will be little ammonium oxidation, and nitrification ceases in the total absence of oxygen. Even though oxygen is essential, nitrification can occur readily down to about 0.3 ppm dissolved oxygen (Reddy and Patrick, 1982).

The optimum pH of nitrification is 8.0, and activity decreases rapidly below pH 7 (Alexander, 1965). The relationship between nitrification and soil pH has been studied by many researchers (Dancer et al., 1973; Pang et al., 1975; Reid and Waring, 1979). They found

that nitrification increased with increasing pH in the approximate range of 4.6 to 6.7. Pang et al. (1975) found that nitrification rate was related to the initial pH of soils and the number of Nitrosomonas and Nitrobacter present in soils. Low nitrifying capacity was observed in limed acid soil, which they attributed to the adverse effect of liming on the Nitrosomonas population. They also observed that soil with high initial pH maintained a high nitrifying capacity even when acidified to pH 5.5; however, the initiation of nitrification was delayed by the reduction in pH. The rate of nitrification is also affected by pH in soil-water systems. In laboratory soil-water column studies, Erickson (1978) showed that the rate of nitrification occurring at the soil-water interface was tripled by increasing pH from 4.7 to 7.0 through the addition of lime.

4. Denitrification. Denitrification is one of the major mechanisms by which nitrogen is lost from a flooded soil or sediment. A small group of bacteria (Payne, 1973; Brezonik, 1978) reduce nitrate to  $N_2O$  and  $N_2$  (dissimilatory reduction or denitrification). In denitrification, nitrate serves as a terminal electron acceptor in place of oxygen during the oxidation of the substrate. Among the facultative anaerobic bacteria capable of this reaction are species in the genera Pseudomonas, Achromobacter, Bacillus, and Micrococcus.

Denitrification is now regarded as a four step sequence as follows:



Four separate and identifiable enzyme complexes are involved in the denitrification process (Payne, 1973). Nitrate reductase has been isolated from bacterial systems, with iron and molybdenum as specific cofactors.

This enzyme reduces nitrate to nitrite, a two electron transfer. The enzyme responsible for the reduction of nitrite to nitric oxide is nitrite reductase. Nitric oxide and nitrous oxide reductases are involved in the rest of the reduction steps. Even though there is some evidence on the isolations of these two enzymes, almost nothing is known about electron transport at the last reduction levels. According to Bandurski (1965), with the exception of the terminal enzymes, the electron transport system of facultative anaerobes is identical under aerobic and anaerobic conditions.

Denitrifiers require a source of hydrogen ions and electrons to reduce nitrate and carbon sources for cellular growth. These requirements can be satisfied by the presence of organic matter. The significance of organic matter in the denitrification process has been studied extensively (Bremner and Shaw, 1958; Focht et al., 1979; Beauchamp et al., 1980; Krottje, 1980; Reddy et al., 1978; Burford and Bremner, 1975; Wickramasinghe and Talibudeen, 1981). Rate of nitrate disappearance from soils under anaerobic conditions increases with organic matter content as shown by addition of glucose or other carbon sources (Bremner and Shaw, 1958; Reddy et al., 1978; Wickramasinghe and Talibudeen, 1981; Focht et al., 1979). A few studies have attempted to correlate various indexes of organic matter availability to denitrification rates. Stanford et al., (1975) reported that denitrification correlated better with glucose carbon extracted by boiling 0.01M  $\text{CaCl}_2$  solution for one hour, while Burford and Bremner (1975) found mineralizable carbon and soluble carbon provided better correlation with the denitrification rate than total organic carbon. In an attempt to determine a suitable method of estimating available carbon for soil denitrifiers, Beauchamp

et al. (1980) found that total organic carbon gave highest correlation with denitrification rate. Using the relationship between soil organic matter content, pH, and denitrification, Krottje (1980) developed a predictive equation for denitrification rates in many of Florida's wetland soils.

The influence of environmental factors, such as temperature, pH, and oxygen level on denitrification rate has been extensively reviewed by Bremner and Shaw (1958), Delwiche (1966), Nommik (1956), and Brezonik (1978). Denitrification rate increases with increasing temperature from 5 to 60°C. Stanford et al. (1975) reported a  $Q_{10}$  of about 2 between 15 and 35°C for denitrification in soil. The optimum pH for denitrification is between 7 and 8, and rates decline rapidly under acidic conditions. Denitrification rates also increase with decreasing oxygen level.

Denitrification is essentially an anaerobic process. In a water system, denitrification can occur in the presence of low levels of oxygen only if the microorganisms are metabolizing in an anoxic microzone such as within suspended particles. This aspect of denitrification has been reviewed extensively by Painter (1970) and Brezonik (1977). Nelson et al. (1973) reported that less than 1 ppm dissolved oxygen and greater than 50 ppm dissolved organic carbon were necessary for denitrification in water.

Koike et al. (1972) showed a significant effect of nitrate concentration on denitrification in a brackish Japanese lake. At a concentration of 700  $\mu\text{g NO}_3^- \text{-N/l}$ , the rate of denitrification was 2.86  $\mu\text{g/l/day}$ , whereas at a lower concentration of 70  $\mu\text{g NO}_3^- \text{-N/l}$ , the rate was 0.67  $\mu\text{g/l/day}$ . Van Kessel (1977) found that the denitrification rate in

sediment was dependent on nitrate concentration in the overlying water, following first-order kinetics at lower concentrations ( $0.100 \text{ mg NO}_3^- \text{-N/l}$ ), but it gradually became independent (zero-order kinetics) of the nitrate concentration at higher levels ( $100 \text{ to } 500 \text{ mg NO}_3^- \text{-N/l}$ ).

Several studies have been made on the distribution and transformation of nitrate in anoxic sediment (Vanderborcht and Billen, 1975; Patrick and Reddy, 1976; Kemp and Mudrochova, 1972). Grundmanis and Murray (1977) have studied movement of nitrate from bottom water and/or oxic sediment to anoxic sediment in more detail. They suggested that nitrate can enter anoxic sediment by three mechanisms: 1) diffusion, 2) burial of bottom water with accumulating sediment, and 3) advective exchange of interstitial water with bottom water. Denitrification in surficial sediments is likely to be an important nitrogen sink since sediments are reduced and rich in organic matter. Rates of denitrification in sediment-water systems are difficult to measure directly, because transport processes are involved and it is difficult to sample the sediment without affecting these processes. Vollenweider (1968), Anderson (1974), Larsen (1975), and Messer and Brezonik (1977) used a mass balance approach to obtain evidence for the importance of sediment denitrification as nitrogen sink in lakes. Messer and Brezonik (1977) estimated that 34% of the annual nitrogen input was denitrified in Lake Okeechobee sediment.

#### C. Role of Nitrification-Denitrification Reactions in Nitrogen Removal in Wetland Systems.

Mechanisms responsible for nitrogen removal in wetland systems include nitrification-denitrification reactions, plant uptake, and

microbial assimilation (immobilization). However, nitrification-denitrification reactions are generally considered to be the major mechanism for removal of inorganic nitrogen in wetland systems (Fetter et al., 1978; Boyt et al., 1977; Zoltek et al., 1979; Small, 1978; Reddy et al., 1980b; Chen and Patrick, 1981). Nitrification and denitrification can occur simultaneously in flooded soils (Patrick and Reddy, 1976) and in sediments (Grundmanis and Murray, 1977; Koike and Hattori, 1978). Nitrification can occur in the aerobic water column or the oxidized surface soil layer and the nitrate produced is subject to denitrification after diffusion into the deeper anaerobic zone of soils and sediments and in anoxic waters. These processes are illustrated in Figure 3.

In wetland ecosystems, the rate of denitrification is also affected by thickness of the oxidized soil layer, depth of overlying water, and the rate of nitrate diffusion to the active zone of denitrification in addition to the factors mentioned earlier. The oxidized soil layer is the zone in which nitrification takes place; therefore, if the oxidized soil layer is thick, the rate of nitrification would be faster than in a thinner oxidized soil layer (Patrick and Reddy, 1976). Consequently, higher amounts of nitrate could be removed by denitrification. Studies by Reddy et al. (1976) also indicated that the rate of nitrification is one of the factors controlling nitrogen loss from flooded soils. Using  $^{15}\text{N}$  labelled ammonium added to flooded soils having different atmospheric oxygen concentrations, Patrick and Reddy (1976) found that the nitrification rate was reduced where oxygen was limiting, resulting in a reduced amount of nitrate available for denitrification.

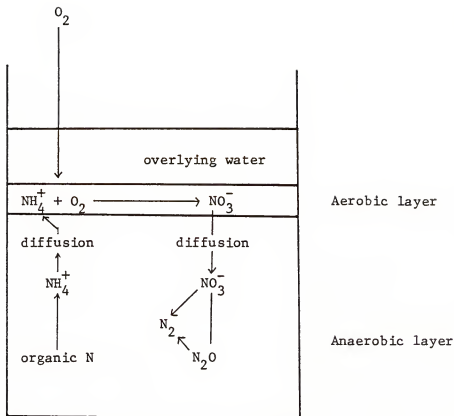


Figure 3. Processes involved in the sequential conversion of organic nitrogen to elemental nitrogen in sediments. Ammonium is released from organic matter and diffuses upward into the aerobic sediment layer where it is nitrified. Nitrate produced from this reaction diffuses down into the anaerobic layer where denitrification takes place. Oxygen diffusing into the sediment from the water column creates an aerobic zone that is required for nitrification to occur (Patrick and Reddy, 1976).



In earlier experiments, Tusneem and Patrick (1971) showed that the total amount of nitrogen lost usually exceeds the amount of nitrate and ammonium present in the oxidized soil layer at any one time. This large nitrogen loss can be attributed to the diffusion of ammonium from the anaerobic soil layer to the aerobic soil layer. Removal of ammonium by nitrification in the aerobic layer creates a concentration gradient which causes ammonium in the deeper anaerobic layer to diffuse upward to the aerobic layer where it undergoes nitrification. The importance of ammonium diffusion in nitrogen loss from flooded soils was also recognized by Reddy et al. (1976). In their study, they estimated that more than 50% of total ammonium was lost by diffusion of ammonium from the anaerobic soil layer to the aerobic soil layer. Production of nitrate by nitrification also creates a concentration gradient which causes nitrogen to diffuse down toward a nitrate-free anaerobic layer where it is denitrified (Patrick and Reddy, 1976). Reddy et al. (1978) found that nitrate diffusion also plays a significant role in determining denitrification rate. Their studies indicated that nitrate disappearance is a first-order reaction when nitrate loss involved both nitrate diffusion from the overlying water and denitrification, where in the system without overlying water nitrate disappearance was a zero-order reaction.

Since many laboratory experiments demonstrated that a significant amount of nitrogen is removed through nitrification-denitrification in simulated wetland or flooded soil systems, researchers have proposed the use of shallow reservoirs, flooded organic soils, and wetland systems for waste water treatments (Reddy and Graetz, 1981; Bartlett et al., 1979; Lance, 1972; Chen and Patrick, 1981).

## II. Phosphorus Removal from Agricultural Drainage Water by Wetland Soils

Agricultural lands, either croplands or animal farming areas, have been shown to contribute phosphorus to drainage water (Ryden et al., 1973; Neilsen and MacKenzie, 1977). Phosphorus levels in drainage water from agricultural land can be affected by time, amount and intensity of rainfall, rates of infiltration and percolation, slope, soil texture, nature and distribution of native soil phosphorus, cropping practice, crop cover density, etc. (Ryden et al., 1973). Taylor et al. (1971) estimated that about 0.07 kg P/ha/yr as total phosphorus was lost from a 50% permanent pasture and 50% winter wheat-meadow area in Coshocton, Ohio. Olness et al. (1980) studied fertilizer nutrient losses from rangeland watersheds in central Oklahoma. They found that total phosphorus concentration in surface runoff from fertilized watersheds (75 kg P/ha) were 10 to 20 times greater than from unfertilized watersheds, and total soluble phosphorus concentrations were 200 to 600 times greater one week after fertilization and 4 days after an intense thunderstorm delivered about 9.4 cm of rain. They also estimated that 2.9 and 3.6 kg P/ha of fertilizer was lost 1 week after fertilization from rotation-grazed and continuously grazed watersheds, respectively.

Phosphorus lost from agricultural lands can increase the rate of biomass production in surface water. It has been found that even soluble phosphorus concentration as low as 10  $\mu\text{g P/l}$  accelerated algal growth in standing bodies of water (Biggar and Corey, 1969; Holt et al., 1970). Therefore, control of phosphorus movement from these lands becomes necessary to limit eutrophication. Some researchers suggested

that part of the phosphorus released to drainage water can be readsorbed by soils during transport (Burwell et al., 1974). Several studies have found that the soluble phosphorus concentration of drainage water decreases during transport from agricultural lands due to sorption of phosphorus by suspended sediment and underlying soils (Taylor and Kunishi, 1971; Sharpley and Syers, 1979; Neilsen and MacKenzie, 1977; Sharpley et al., 1981).

In recent years, several workers have used wetland soils for reducing phosphorus levels of waste water effluents and agricultural drainage water (Fetter et al., 1978; Boyt et al., 1977; Tilton and Kadlec, 1979; Reddy and Graetz, 1981). The capacity of the soil or sediment to release orthophosphate to a solution low in phosphorus and to sorb it from a solution high in phosphorus is a major factor in controlling the amount of dissolved inorganic orthophosphate in flooded soils, swamps or shallow reservoirs. A wide variation has been reported in the ability of different sediments or soils to sorb phosphorus (William et al., 1970; Shukla et al., 1971). Some soils are capable of sorbing large amounts of phosphorus, but some appear to be almost saturated.

#### A. Soil Components Responsible for Phosphate Sorption.

It is generally believed that hydrous oxides of iron and aluminum, and edge aluminum of clay minerals are mainly responsible for phosphate sorption in acid soil (Chu and Sherman, 1953; Saunders, 1965). Sorption of inorganic phosphorus by calcium carbonate has also been demonstrated in calcareous soils (Cole et al., 1953; Holford and Mattingly, 1975). Shukla et al. (1971) suggested that a gel complex of hydrated

iron containing small amounts of aluminum oxide, silicon hydroxide, and organic matter was a major phosphorus sorbing component in lake sediments, especially under reduced conditions.

1. Iron and aluminum compounds. It has been shown that phosphorus in soil solution is sorbed by short-range order oxides and hydrous oxides of iron and aluminum in soils (Williams et al., 1958; Hsu, 1964; Saunders, 1965; Syers et al., 1971; Khalid et al., 1977). The amount of phosphate sorbed in these reactions depends on temperature, time of reaction, phosphate concentration, and pH of the solution. In acid mineral soils, the exchange complex contains appreciable amounts of absorbed aluminum and smaller but significant amounts of iron and manganese. Phosphates combine with these ions to form insoluble compounds of aluminum, iron, and perhaps manganese. The resulting compounds may be precipitated from solution or adsorbed on the surface of iron and aluminum oxides or on clay particles. Wild (1950) concluded that the formation of iron and aluminum phosphate in soil would be expected, based on the following evidence:

(i) Correlation has been established between phosphate sorption and the amounts of iron and aluminum in soils.

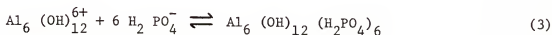
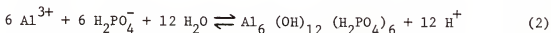
(ii) Some studies showed decreases in sorption of phosphate under acid conditions by addition of 8-hydroxy quinoline to soil (Ghani, 1943). As 8-hydroxy quinoline was thought to block active iron and aluminum, this was taken as evidence for the formation of iron and aluminum phosphates.

(iii) Doughty (1930) observed considerable increases in phosphate sorption when a peat soil was saturated with iron and aluminum by

leaching with ferric chloride and aluminum chloride. The maximum sorption was at pH 2.5 following the ferric chloride treatment, and at pH 4.0 after leaching with aluminum chloride.

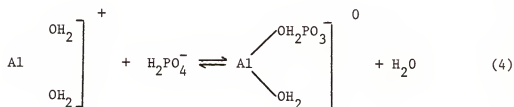
(iv) Teakle (1928) observed the effect of pH on the precipitation of iron and aluminum phosphate. With iron, precipitation of phosphate was greatest at pH 3.0, and with aluminum, at pH 6.8.

Hsu (1965) proposed an approach to describe the fixation of phosphate by aluminum and iron in acidic soils. He suggested that in principle, precipitation and adsorption result from the same chemical force (the attractive force between phosphate and aluminum (or iron)). Precipitation refers to a process in which phosphate precipitates as difficultly soluble compounds with aluminum or iron in acid soils or with calcium in neutral or alkaline soils. Adsorption is a special case of precipitation in which aluminum (or iron) remains as a constituent of the original phase but reacts with phosphate by use of residual force on the surface. Occurrence of either precipitation or adsorption is dependent on the size of iron or aluminum polymer, pH, and the solution phosphate concentration. Hsu (1965) suggested that in a moderately acidic medium (such as pH 4) with a high phosphate concentration, the reaction process may be a typical precipitation following Equations 2 and 3:

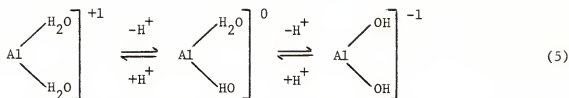


In a slightly acidic to neutral (such as pH 6 to 7) dilute phosphate solution, short-range order (amorphous) oxides and hydrous oxides of aluminum are stable and phosphate is adsorbed on the surface. Hsu (1965) also concluded that whenever phosphate fixation occurs, it must be due to the attraction between phosphate and aluminum (or iron). Precipitation occurs when phosphate removes aluminum (or iron) completely from the lattice and reprecipitates as a new phase. Adsorption occurs when phosphate can break only part of the Si-O-Al or Al-OH linkage, leaving aluminum (or iron) still in the lattice.

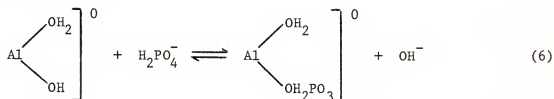
Recent evidence for ligand exchange in soils comes from studies of competitive adsorption of anions, adsorption isotherms, and change in adsorption at different pH values (Obihara and Russell, 1972; Rajan et al., 1974; Parfitt, 1977; Ryden et al., 1977). Studies of surface charge and ligand exchange at constant pH using hydrous alumina by Rajan et al. (1974) indicated that monovalent phosphate is adsorbed on positive sites displacing water that was coordinated to the oxide surface, thus adding a negative charge to the surface without increasing the concentration of hydroxyl ions in the solution as shown in Equation 4.



As pH increases, some of the water molecules that were coordinated to the oxide surface are placed by hydroxo groups (Al-OH) (see Equation 5).

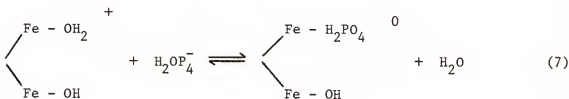


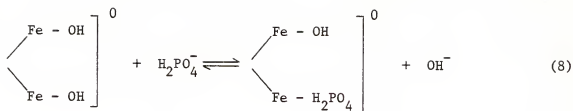
In contrast, monovalent phosphate is adsorbed on the surface by exchanging with the hydroxo groups, without affecting the surface charge but with releasing equivalent amounts of hydroxyl ions into the solution as shown in Equation 6.



Rajan et al. (1974) also found that adsorption took place mainly by displacing aquo groups ( $\text{Al}-\text{H}_2\text{O}$ ) and hydroxo groups at low and high phosphate concentration. More phosphate was still adsorbed, even after the adsorption sites (aquo and hydroxo groups) were saturated. Additional adsorption evidently occurred by disruption of hydrous oxide polymers into smaller units which in turn act as new adsorption sites.

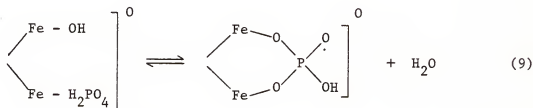
Reaction of phosphate with hydrous oxides of iron is similar to their aluminum counterpart, as described by Equations 7 and 8, depending on the degree of protonation of single coordinated-OH groups (Berkheiser et al., 1980).





Ryden et al. (1977) studied phosphate sorption on iron oxide gel, and proposed three mechanisms for phosphate sorption as follows:

(1) chemisorption at protonated surface sites, which can be described by Equation 7; (2) chemisorption by replacement of surface hydroxyls, which can be described by Equation 8; (3) sorption of phosphate as a potential determining ion, which could occur by the condensation reaction given in Equation 9.



Parfitt et al. (1975) have also demonstrated that the mechanism for phosphate sorption on dried iron gel surface was the formation of a binuclear bridging  $\text{FeOP}(\text{O}_2)\text{OFe}$  complex. Since the mechanisms for phosphate sorption on iron and aluminum compounds are very similar, it has been difficult to separate the effect of iron and aluminum on phosphate adsorption.

2. Silicate clays. The reaction of phosphates with silicate clays has been suggested to partially explain phosphorus sorption by soils. Soil clays are composed of layers of silica and alumina combined to form silica-alumina sheets. The two principal types of clay minerals



are 2:1 (two silica sheets with one alumina sheet in the middle) and 1:1 (one silica sheet and one alumina sheet). Generally, soil with high 1:1 clay minerals can fix more phosphate than soil with high 2:1 clay minerals. It has been suggested that phosphate ions may combine directly with these clays by (1) replacing a hydroxyl group from an aluminum atom located at the crystal edge when phosphate concentration is low ( $<0.3 \times 10^{-3} \text{M}$ ) (Muljadi et al., 1966; Rajan et al., 1974; Parfitt et al., 1975), and (2) displacing clay structural silicate when phosphate concentration is high (Low and Black, 1950; Rajan, 1975).

Mechanisms of phosphate sorption by clay have been found to be similar to those for sorption by oxyhydroxide compounds of iron and aluminum (Berkheiser et al., 1980; Hingston et al., 1967, 1974; Kafkafi et al., 1967). Hingston and several coworkers (1967, 1974) have elaborated the hydroxyl-exchange hypothesis of phosphate adsorption at the edge faces of kaolinite and the surface of gibbsite and goethite. This hypothesis has also been referred to as phosphate adsorption by ligand exchange, or specific adsorption of phosphate, which has been discussed earlier.

3. Calcium compounds. Two mechanisms involved in phosphate fixation by calcium compounds in soils are adsorption and precipitation. The occurrence of either adsorption or precipitation reactions is dependent on the concentration of phosphate in the soil solution. Boischot et al. (1950) and Cole et al. (1953) indicate that the reactions between calcium carbonate and added soluble phosphate fertilizers in calcareous soils consist of rapid monolayer sorption on the surface of calcium carbonate at low phosphorus concentration, and the precipitation of dicalcium phosphate or a compound with similar

properties at high phosphorus concentration in the vicinity of fertilizer particles. Stumm and Leckie (1971) concluded that the adsorption reaction involves three steps: (1) chemisorption of phosphate accompanied by heterogenous formation of nuclei of amorphous calcium phosphate, (2) a slow transformation of these nuclei into crystalline calcium phosphate, and (3) crystal growth of calcium phosphate.

Phosphate adsorption on calcium carbonate surfaces is generally described by a Langmuir equation (Cole et al., 1953; Kuo and Lotse, 1972; Holford and Mattingly, 1975). Griffin and Jurinak (1973, 1974) used a two region Langmuir isotherm equation to describe adsorption isotherms of phosphate on calcite. They found that the break in the slope of two distinct linear portions of the Langmuir plot corresponds to the division between formation of octacalcium phosphate and hydroxylapatite. Furthermore, they showed that the first reaction, representing the adsorption of phosphate, was second-order. The second reaction, which was considered to be associated with the surface arrangement of phosphate clusters into calcium phosphate heteronuclei was first-order. However, Kuo and Lotse (1972) developed a second-order kinetic equation based on both the change in phosphate concentration in solution and the surface saturation of the phosphate during the adsorption process. Kuo and Lotse (1972) and Hsu (1968) made similar conclusions that phosphate ions are adsorbed by displacing coordinating water molecules rather than hydroxyl groups on the surface of calcium ions.

In the studies on the reaction between calcium carbonate and phosphate ions Mattingly (1975) found much of the phosphate adsorbed rapidly on the surface as a monolayer. Therefore, the amount of adsorbed phosphate and the equilibrium concentration of phosphate vary with the

surface area of calcium carbonate used. Holford and Mattingly (1975) also illustrated the importance of surface area of calcium carbonate molecules based on significant and positive correlation between calcium carbonate surface and low-energy adsorption capacities (400-633  $\mu\text{g P/g}$ ).

Since the retention of phosphate by calcium carbonate is well-recognized, Brown (1980, 1981) has proposed the use of calcareous materials for phosphorus immobilization from domestic waste water. He found that calcium phosphate precipitation from slightly super-saturated solutions can be induced by addition of hydroxyapatite seed crystals. This method involving precipitation of phosphorus from waste water as either hydroxyapatite or fluoroapatite in soil before it enters surface water can be potentially cost-effective in preventing cultural eutrophication.

4. Organometallic complexes. The sorption of phosphate by organometallic complexes has been recognized for some time, but not much is known about the chemistry of these interactions, especially the relative stability of the complexes and the dynamics of their transformation in soils. As early as 1930, Doughty (1930, 1935) gave evidence that retention of phosphate is due to its reaction with iron, aluminum, and calcium ions which are associated with organic matter. Later more workers illustrated that phosphate can react with metal ions to form different types of complexes in the presence of organic ligands (Lincoln and Strank, 1968; Bohn and Peech, 1969; Weir and Soper, 1962; 1963; Levesque and Schnitzer, 1967). According to Weir and Soper (1962, 1963), the complex between iron and organic groups in humic acid extracts of soil organic matter has the capacity to retain phosphate

ions, and this retention is a function of pH. Finally, they concluded that organic soils can fix phosphorus and the fixation increase with additions of iron or aluminum.

Levesque and Schnitzer (1967) used differential thermogravimetric analysis, infrared spectroscopy, and extractability techniques to study the interactions involving organic matter, metal, and phosphorus in soils. They concluded that phosphorus in the low and medium complexes (based on the amount of phosphorus present in the complexes) occurred as orthophosphate bonded through the metal or fulvic acids, whereas in the high phosphorus complex a considerable proportion of the phosphorus occurred as metal phosphate mixed physically with fulvic acid-metal complexes.

Sinha (1971) observed that stable undissociable organometallic phosphates were formed only when humic and fulvic acids contained complexed iron or aluminum. He also suggested that phosphate ions may be acting as ligands in organometallic compounds, as indicated by a relatively higher proportion of phosphate than iron in these compounds.

Recently, Bloom (1981) studied phosphorus adsorption by an organic matter-Al complex in acid soils using an Al-peat complex. Adsorption isotherms show that the Al-peat complex strongly adsorbs orthophosphate ions and that adsorption is a function of pH. More importantly, this study demonstrates the significant role of Al-organic matter complex in phosphate adsorption in acid surface soil, especially in mineral soils with high organic matter contents.

## B. Retention of Phosphorus by Flooded Soils

The extent of phosphorus retention by soils depends upon chemical, physical, and mineralogical properties of the soils. When a soil is flooded, some of these soil properties (especially chemical properties, i.e., pH and redox potential) are changed. Consequently differences between phosphorus retention by flooded soils and by terrestrial soils have been observed by many workers (Hsu, 1964; Ryden et al., 1973; Ponnamperna, 1972; Khalid et al., 1977; Patrick and Khalid, 1974). Hsu (1964) observed an increase in inorganic phosphorus sorbed by soils from 60 to 99  $\mu\text{g P/g}$  soil after 1 year of continuously wet incubation. The increased sorption was attributed to release of iron to solutions from crystalline phases due to the development of localized reducing conditions during incubation, and reprecipitation of "ferric hydroxide" on contact with more aerobic conditions. Shukla et al. (1971) suggested that a gel complex of hydrated iron oxide or the short-range order forms of iron, transformed from a crystalline form in noncalcareous sediment, is responsible for sorption of added phosphorus by noncalcareous sediment. Using different extractants, Harter (1968) extracted sorbed phosphorus from sediment and found that the sorbed phosphorus was in the forms of both iron and aluminum phosphate.

According to Patrick and Khalid (1974), anaerobic soils or flooded soils released more phosphate to solutions low in soluble phosphate and sorbed more phosphate from solutions high in soluble phosphate than did aerobic soils. They suggested that the difference in behavior of phosphate under aerobic and anaerobic conditions is due to the transformation of ferric oxyhydroxide to more reactive ferrous compounds in anaerobic soils. Later Khalid et al. (1977) found a close

relationship between phosphate sorbed and oxalate extractable iron (the short-range order forms of iron) under reduced conditions, which indicates that the short-range order forms of Fe or the amorphous oxides and hydroxides of iron play a significant role in phosphorus retention by flooded soils. These results also confirm the study by Shukla et al. (1971) as mentioned earlier.

Desorption of sorbed added inorganic phosphorus by flooded soils has also been investigated (Williams et al., 1970; Shukla et al., 1971). Williams et al. (1970) found that calcareous sediment with low oxalate extractable Fe sorbed less inorganic phosphorus and desorbed a higher proportion of sorbed phosphorus than the noncalcareous sediments investigated. Shukla et al. (1971) also suggested that oxalate extractable iron seemed to be more important than calcium carbonate in determining the amount of added phosphorus sorbed by calcareous sediments.

It is well documented that more dissolved inorganic phosphorus is released from flooded soils or sediments under anaerobic than aerobic conditions (Mortimer, 1941; Hayes, 1964; Olsen, 1964; Li et al., 1972; Stumm and Leckie, 1971). Ponnampetuma (1972) suggested a few reactions which may cause the increase in concentration of water-soluble phosphorus when acid soils are flooded. These reactions are (1) hydrolysis of iron (III) and aluminum phosphates, (2) release of phosphorus held by anion exchange on clay and hydrous oxides of iron (III) and aluminum, and (3) reduction of iron (III) to iron (II) with liberation of sorbed and chemically bonded phosphorus. The occurrence of the first two reactions can be attributed to the pH increase which generally occurs in reduced soils. In alkaline soils the increase in

soluble phosphorus is a consequence of the decrease in pH of these soils on flooding. According to Stumm and Morgan (1970), the solubility of hydroxylapatite increases as pH decreases.

Syers et al. (1973) suggested that the level of dissolved inorganic phosphorus in the soil solution of flooded soils and sediments should be controlled by sorption and desorption reactions. Niriagu (1972) and Niriagu and Dell (1974) also suggest that phosphorus is retained by the solid phase in sediment water systems by a sorption reaction rather than by precipitation reaction, which can be confirmed by the extensive and rapid exchange in native and sorbed added inorganic phosphorus in aerobic and anaerobic sediments observed by Li et al. (1972).

#### C. Methods for Determining Phosphate Adsorption

Adsorption curves have been used widely to determine phosphorus fertilizers requirements of different types of soils (Beckwith, 1965; Ozanne and Shaw, 1967, 1968; Kunishi and Vickers, 1980; Reddy et al., 1980a). From the adsorption curve (a plot of sorbed phosphorus vs solution phosphorus), the equilibrium phosphorus concentration (EPC) values can be obtained. The EPC is the concentration that is supported by soil samples when in contact with an ambient solution such that no phosphorus is either gained or lost (White and Beckett, 1964). Recently, the EPC became an important parameter to be determined as it describes the adsorption characteristics of soils utilized for disposal of animal wastes (Reddy et al., 1980a) and in shallow reservoirs used for waste water treatment (Reddy and Graetz, 1981).

An adsorption isotherm describes the equilibrium relationship between the amounts of adsorbed and dissolved species at a given temperature. Many workers have studied phosphate adsorption isotherms on soil or various soil components and then have attempted to fit the results to Freundlich or Langmuir adsorption isotherm equations (Olsen and Watanabe, 1957; Woodruff and Kamprath, 1965; Ryden et al., 1977; Munns and Fox, 1976; White and Taylor, 1977). The adsorption equations developed by Freundlich and Langmuir to quantitatively describe gas adsorption by solids have been used with some solid-liquid systems; however, there are some flaws in using these equations in such systems, which will be discussed later.

The Freundlich adsorption isotherm is expressed by  $X = aC^{1/n}$  where  $X$  is the amount of phosphorus adsorbed per unit weight of soil,  $C$  is phosphorus concentration in solution and  $a$  and  $n$  are constants that vary with soils. The equation may also be written as  $\log X = \log a + 1/n \log C$ . This isotherm implies that the energy of adsorption decreases exponentially with increasing saturation of the surface and that a plot of  $\log X$  against  $\log C$  would yield a straight line. The exponent  $1/n$  in the first equation was found to be closely related to the exchangeable aluminum in acid soils, with a mole ratio of 1 P to 6 Al (Fitter and Sutton, 1975).

The Langmuir equation is the most widely applied and may be written in linear form as  $C/X = C/X_m + 1/KX_m$  where  $X$  and  $X_m$  are the amount of phosphorus adsorbed per unit weight of soil and adsorption maximum, respectively,  $C$  is the phosphorus concentration at equilibrium and  $K$  is the constant related to the bonding energy.



Assumptions for deriving the Langmuir equation are: localized monolayer adsorption (adsorbate nonmobile), heat of adsorption (Q) constant over the entire monolayer, no lateral interactions of adsorbate molecules,  $X_m$  and K are independent of temperature, rate of desorption set equal to rate of adsorption, the maximum adsorption possible corresponds to a complete monomolecular layer. Straight line isotherms are obtained when results from a limited concentration range are plotted according to the Langmuir equation. In some cases the data can best be fitted with two straight lines, and this suggests the existence of two populations of adsorption sites which have a widely different affinity for phosphorus. As a result, the Langmuir equation was modified for two groups of adsorption sites. Muljadi et al. (1965), Syers et al. (1973), Rajan (1975), and Rajan and Fox (1975) have used a binary Langmuir equation in the form of  $X = (X_{m1} - X_1/K_1C) + (X_{m2} - X_2/K_2C)$  where the subscripts represent the two different groups of phosphorus adsorption over a wider concentration range. Holdford et al. (1974) used a binary Langmuir equation for describing phosphorus adsorption from solution containing  $10^{-3} M$  P. They observed that over 90% of the native adsorbed phosphorus occurred on the high energy surface (surface with high affinity for phosphorus) in most of the soils investigated.

There are some advantages in using the regular Langmuir equation to describe the adsorption of phosphate by soils. A major advantage, as pointed out by Olsen and Watanabe (1957), is that it is possible to calculate an adsorption maximum and a relative binding energy term for phosphorus adsorption. In recent years, failures of the Langmuir equation have been observed even with low phosphorus concentrations (Gumary,

1970; Bache and Williams, 1971; Ballaux and Peaslee, 1975; Harter and Baker, 1977). Harter and Baker (1977) observed the curvilinear nature of the  $C/X$  VS  $C$  plots due to not considering the effect of desorbed ions in the equilibrium solution. They also found that  $K$  is not simply related to the bonding energy of the adsorbed ion, but to the ratio of adsorbed and desorbed ion bonding energies. Furthermore, Veith and Spósito (1977) and Harter and Baker (1977) recommended that the Langmuir equation can be used only on the basis of a statistical analysis, for example, to calculate the adsorption maxima which are subsequently correlated with the chemical, mineralogical, and/or physical properties of the soils. The Langmuir equation should not be used to evaluate adsorption dynamics of soils.

### III. Nutrient Availability from Decaying Vegetation in Wetland Ecosystems

Vegetation plays an important role in nutrient cycling in wetland ecosystems. Ecologically, plants act as primary producers taking up or assimilating inorganic nutrients in the soil and water. Based on this alone, many workers have proposed the use of wetlands or similar systems to remove nutrients from nutrient-laden water (Boyd, 1976; 1970a; 1970b; Boyd and Hess, 1970; Boyt et al., 1977; Chen and Patrick, 1981). Wetlands are typically highly productive ecosystems (Carter, 1973). This high productivity is partially attributed to the wetland's acting as a filter to trap nutrients from the water and store them in plant biomass. The marsh plant Spartina alterniflora was found to recover slightly over 50% of the added nitrogen in the plant shoots and roots after 4 months (Buresh, 1978). The assimilated nutrients are later

released back to the water during the plant decomposition process. These regenerated nutrients can either be taken up by microorganisms involved in further decomposition of plant material, trapped or adsorbed by sediment, or again be assimilated by plants or algae.

#### A. Regeneration and Fate of Plant Nutrients from Decomposing Aquatic Plants

In recent years, several studies on the regeneration and fate of plant nutrients as an aquatic plant decays have been reported (Boyd, 1970; Nichols and Keeney, 1973; De la Cruz and Gabriel, 1974; Strange, 1976; Puriveth, 1980; Davis and Van der Valk, 1978; Gaudet, 1977; Hachney and De la Cruz 1980; Hill, 1979; Reddy and Sacco, 1981). Upon the death of the plant, there appear to be two distinct phenomena that occur with regard to dry matter loss and nutrient release (Boyd, 1970b; Hill, 1979; Hunter, 1976; Puriveth, 1980). The first phase is a very rapid loss of dry matter and nutrients shortly after plant death as a result of solubilization of organic matter. This appears to be primarily a physical process rather than a microbial decomposition process. Boyd (1970b) found greater weight loss of Typha latifolia in bags anchored on the surface of the mud than from bags suspended above the water surface during the first 20 days of decomposition and he attributed it to solubilization of substances rather than microbial activity. In a study on decomposition of aquatic macrophytes by Hill (1979), 21 to 60% of original dry weight was lost during the first 8 days of decomposition due to rapid leaching of soluble materials. Puriveth (1980) also found an abrupt decrease in dry weight and nutrients in decomposing emergent macrophytes in a Wisconsin marsh during

the first month of decomposition. He further observed that chemical characteristics of the surrounding medium appear to have little effect on this first phase.

The second phase is a slower process apparently related to microbial decomposition processes and results in a continued loss of dry matter while nutrient content may decrease or increase depending on the nutrient levels of the plant material and the surrounding medium. Some workers observed that 100% of the nitrogen, phosphorus, and carbon was lost from decaying aquatic plant tissue within 50-60 days (Hill, 1979; Jewell, 1971). However, several studies also indicated an increase in nutrient content, especially nitrogen, of decomposing plant material which is generally thought to be due to immobilization by decomposer populations (Puriveth, 1980; Nichols and Keeney, 1973; Hynes and Kaushik, 1969; Hunter, 1976). This increase or decrease in nutrient content of decaying plant material will be discussed in more detail in the following section.

#### B. Factors Affecting the Rate of Decomposition and Nutrient Release from Decaying Aquatic Plants

Processes determining the rate of decomposition and nutrient release from decaying aquatic plants as suggested by Davis and Van der Valk (1978) are microbial decay, leaching, microbial uptake, and adsorption by sediments. There are several factors controlling these processes, i.e., characteristics of the plant material, characteristics of the water (e.g., aeration, temperature) in which the plant is undergoing decomposition, and the characteristics of underlying sediments.

The major plant material characteristic which has a significant effect on the decomposition rate and the extent of nutrient release is the C/N ratio. Several studies mentioned earlier show that plant tissue with low C/N ratios would be 100% decomposed or all nutrients would be lost from macrophytic tissue, while in plants with high C/N ratios, nitrogen content tends to increase with time during the decomposition process. However, even for plants with low C/N ratios, nitrogen accumulation was observed during the early stage of the second phase of decomposition (Davis and Van der Valk, 1978; Nichols and Keeney, 1973; Puriveth, 1980; Hunter, 1976; Mason and Bryant, 1975). They attributed this increase in nitrogen in decaying plant material to uptake by microorganisms associated with the decomposing tissues. Such uptake indicates that the nitrogen levels in the decomposing plants were too low to support the decomposer populations. These microorganisms must then extract nitrogen from the surrounding water or sediments to compensate for this deficit. Kaushik and Hynes (1971) and Howarth and Fisher (1976) have shown that addition of nitrogen to decomposing plant material resulted in an increased rate of decomposition.

Characteristics of the water, i.e., aeration, temperature, and pH, in which the plant is undergoing decomposition affect the rate of decay. Although organic matter decomposition generally occurs more rapidly under aerobic conditions, the effect of oxygen on decomposition in aquatic systems has been variable. Godshalk and Wetzel (1978) found that decomposition of dissolved organic matter was most rapid under aerated conditions at either 10 or 25°C. Decomposition of water hyacinth was also shown to be faster under aerobic conditions than

under anaerobic conditions (Reddy and Sacco, 1981) while decomposition of water milfoil was more rapid in nonaerated systems (Nichols and Keeney, 1973). Nichols and Keeney (1973) also suggested that decomposition was faster in the nonaerated system because nitrogen was less limiting due to a lower demand for nitrogen (i.e., microorganisms assimilate less carbon per unit of organic matter decomposed) under anaerobic decomposition. In investigations of algal decomposition rates, no significant differences were noted between aerobic and anaerobic conditions (Foree and McCarty, 1970). Decomposition generally increases as temperature increases. Myriophyllum spicatum decomposition in a lake system had a Q<sub>10</sub> of about 3 (Carpenter and Adams, 1979). Significant increases in decomposition rate between 10 and 18°C were also noted by Purvieth (1980). Very little study has been done on the effect of water pH on the rate of aquatic plant decomposition. However, more rapid decomposition could be expected in neutral to slightly alkaline environments as observed in the decomposition of organic matter in soils (Alexander, 1977).

Most investigations have not considered the effect of the underlying sediment on the decomposition rate or the nutrient concentration of the final product. However, Nichols and Keeney (1973) found that decomposition of water milfoil was more rapid when sediment was present apparently due to the capacity of the sediment to supply additional nitrogen in a nitrogen-limiting system. There was also some interaction between sediment and nutrients released from the decaying plant material, particularly in the case of phosphorus with the sediment adsorbing much of the phosphorus released from the plant material. In a study on decomposition of macrophytes in microcosms, Strange (1976)

observed that a considerable amount of phosphorus and nitrogen remained in the refractory portion of the plant residue and was not lost to the water, despite a large reduction of plant biomass.

### CHAPTER III

#### MATERIALS AND METHODS

##### I. Soils

Soil samples used in this study were collected from the Armstrong and Ash Sloughs located in Osceola and Okeechobee Counties, respectively (Figure 4). These sloughs have been developed into experimental retention/detention areas by the Coordinating Council on the Restoration of Kissimmee River Valley and Taylor Creek-Nubbins Slough Basin. Soil samples representing the three major soil types in each slough as indicated in Figures 5 and 6 were collected at various times. Most of the studies were conducted with the soils from Armstrong Slough because the Coordinating Council designated this site to be the major experimental site. The six soil series represented and the descriptions (U.S.D.A. Soil Conservation Service, 1971; 1979) are as follows:

Basinger fine sand--siliceous hyperthermic spodic psammaquent: nearly level, poorly drained, sandy soils formed in thick beds of marine sediments. These soils normally occur in sloughs, along poorly defined drainageways, and in depressions in the flatwoods. The water table is within 25 cm of the surface for 6 to 2 months annually. Depressions are covered with standing water for periods of 6 to 9 months or more in most years. Typically, the surface is about 10 cm of black fine sand over 7.5 cm of dark gray fine sand that contains gray mottles. The subsurface layer is light gray fine sand with dark brown and light brownish gray mottles.





Figure 4. Locations of the experimental sites, Armstrong and Ash Sloughs.

ASH SLOUGH DETENTION AREA  
OKEECHOBEE COUNTY

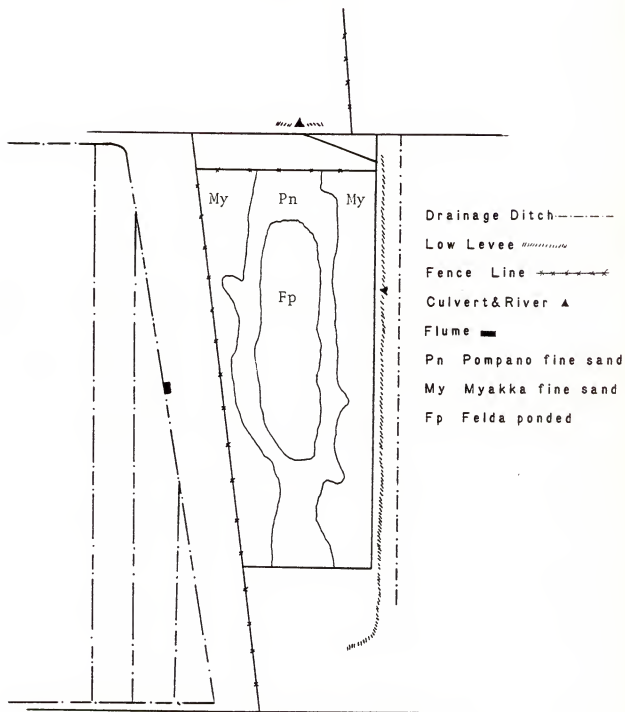


Figure 5. Location of soil types in the retention/detention area at Ash Slough.

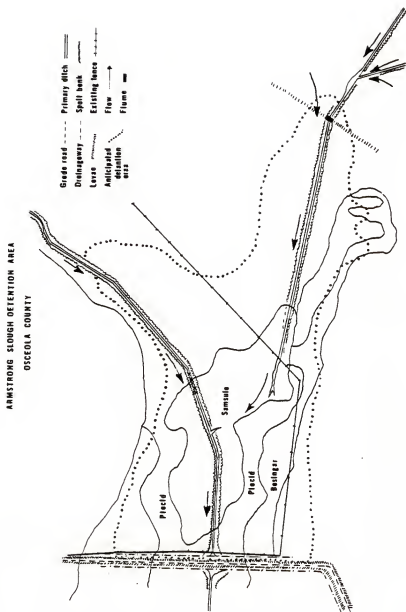


Figure 6. Location of soil types in the Armstrong retention/detention area.

Placid fine sand--sandy siliceous hyperthermic typic humaquepts: nearly level, very poorly drained sandy soils. These soils formed in thick beds of sandy marine sediments. They occur in depressions and swamps throughout the flatwoods. Water stands on the surface for 6 to 9 months or more in most years. The surface layer is about 60 cm thick of fine sand with black over light gray in color. The underlying layer is also fine sand.

Samsula muck--sandy siliceous dysic hyperthermic terric medisaprists: very poorly drained organic soils that formed in moderately thick beds of hydrophytic, nonwoody plant remains and underlying sandy sediments. They occur in freshwater marshes and swamps. Under normal conditions the water is at or above the surface except during extended dry periods. The typical surface layer is muck about 55 cm thick with dark reddish brown over black. Beneath the muck is black fine sand with light gray lenses of fine sand.

Felda ponded--loamy siliceous hyperthermic arenic ochraqualfs: nearly level, sandy soils, very poorly drained. These soils normally occur in depressions that are covered by water most of the year. The surface layer is strongly acid, black fine sand about 10 cm thick above the subsurface layer of slightly acid, grayish-brown and light-gray fine sand.

Pompano fine sand--siliceous hyperthermic typic psammaquents: deep, poorly drained, nearly level soil. It occurs in grassy sloughs and depressions. The water table normally is at a depth of about 5 cm. Typical profile of the surface layer is dark-gray and grayish-brown fine sand about 40 cm thick. The subsurface layer is very pale brown fine sand that has a few to many mottles.

Myakka fine sand--sandy siliceous hyperthermic aeric haplaquods: deep, poorly drained, nearly level, sandy soil in broad flatwood areas. The water table normally is at a depth of about 75 cm. Typical profile of the surface layer is very strongly acid, dark gray fine sand about 15 cm thick. The surface layer is light-gray fine sand above a well-developed organic pan.

## II. Description of Experiments

### A. Denitrification Potential of Soils

1. Denitrification in the absence of overlying water. Surface soil samples representing Basinger, Placid, and Samsula soils were

collected from the Armstrong site on September 3, 1981. Selected soil characteristics are shown in Table 1. These soils were passed through a 0.5 X 0.5 cm screen to remove roots. Fresh, screened soil equivalent to 8 g dry weight was placed in twelve 50 ml bottles. The overlying water (reservoir water) collected from the Armstrong site on the same date was filtered through a Whatman No. 541 filter paper. Each sample was saturated with filtered reservoir water, capped with a rubber septum, and purged with  $N_2$ . These bottles were incubated 4 days to allow all residual nitrate in the system to be denitrified. After this pre-incubation period, 1 ml of solution containing 800  $\mu\text{g N/ml}$  as  $\text{KNO}_3$  was added to 9 bottles of each soil and mixed thoroughly. Three additional samples of each soil were spiked with 1 ml of a solution containing 800  $\mu\text{g N/ml}$  as  $\text{K}^{15}\text{NO}_3$  (99.3%  $^{15}\text{N}$ ). These  $^{15}\text{N}$  samples were to be analyzed on the last day of incubation. These systems were then purged with  $N_2$  gas for one hour. All samples were incubated at  $25^\circ\text{C}$  in an  $\text{O}_2$ -free container. Three samples of Basinger and Placid soils were collected after 0, 1, 3, and 6 days of incubation, while samples of Samsula soil were collected after 0, 1, 2, and 3 days of incubation. Redox potential was measured on the days of sampling. Each sample was extracted with 50 ml of 1N KCl solution for analysis of ammonium, nitrate, and soluble organic nitrogen. Soil samples after extraction were dried at  $40^\circ\text{C}$ , then analyzed for total nitrogen. Appropriate samples were analyzed for  $^{15}\text{N}$ .

## 2. Nitrification and denitrification in soil-water columns.

Soils used in the above experiment were also used in this study. Field moist Placid and Basinger soils were transferred into nine

TABLE 1  
SELECTED CHARACTERISTICS OF SOILS USED IN NITRIFICATION AND DENITRIFICATION EXPERIMENTS

Soil Series	pH	Organic Matter	KCL Extractable		Soil TKN	Double Acid Extractable			
			NH <sub>4</sub> <sup>+</sup>	NO <sub>3</sub> <sup>-</sup>		Ca	Fe	Al	P
		%	µg N/g soil		%	µg/g soil			
Basinger fine sand	3.5	8.8	0.78	0.58	0.25	112	56	209	13.9
Placid fine sand	3.8	20.1	1.39	1.27	0.39	2400	4800	41	1.4
Samsula muck	4.7	94.0	16.60	2.66	1.88	560	120	2496	11.8

replicate plexiglass tubes (5.0 cm I.D.) to obtain a 30-cm long soil column. For the Samsula soil, nine intact soil columns were collected from the Armstrong site. The intact soil columns were collected for Samsula muck because it contained a thick mass of fibrous material below the ooze material which made it difficult to collect a bulk sample. Soil was flooded with reservoir water to a depth of 25 cm and preincubated for a period of one week to insure denitrification of the initial nitrate. At the end of preincubation, 5 ml of a solution containing 2.5 mg N/ml  $[(\text{NH}_4)_2\text{SO}_4]$  with 20%  $^{15}\text{N}$  enrichment] was added to the overlying water of triplicate soil-water columns to measure the nitrification rate in these simulated wetland systems. Overlying water in another triplicate set of soil-water columns was spiked with 5 ml of solution containing 2.5 mg N/ml  $[\text{KNO}_3]$  with 20%  $^{15}\text{N}$  enrichment]. The last set of three soil-water columns was not treated and was used as controls. The top 5 cm of overlying water in each column was continuously bubbled with air. The soil-water columns were incubated at  $23 \pm 2^\circ\text{C}$  for 25 days. Overlying water from each column was sampled at 0, 2, 5, 10, 15, and 25 days, and analyzed for ammonium and nitrate. At the end of the study each soil column was sectioned into 0.5 cm increments to a depth of 10 cm. The soil sections were then extracted with 60 ml of  $1\text{N}$  KCl solution using a leaching method in which the soil sample was placed in a suction filter cup with  $0.45\text{ }\mu\text{m}$  filter membrane and then leached with 20 ml of extractant three times. The KCl extracts were analyzed for ammonium and nitrate. After extraction, soil sections from the top 3 cm of each column were dried at  $40^\circ\text{C}$  and analyzed for total nitrogen.

## B. Phosphorus Removal Potential of Soils

1. Determination of phosphorus adsorption maxima. Samples representing the major soils in the two experimental sites were collected on September 20, 1979. Three of these sites were located at the Ash experimental location and three at the Armstrong location. Major soil series at the Armstrong site were Basinger fine sand, Sammula muck, and Placid fine sand. Felda, Pompano, and Myakka fine sands were the major soils at the Ash site. Bulk samples of the surface layer were used in this study. Subsamples were airdried and analyzed for pH, % organic matter, and double acid extractable aluminum, iron, and phosphorus (Table 2). These samples were taken at an earlier date in approximately the same location as the samples used in the previous nitrogen experiment but some variation in characteristics was noted.

The phosphorus adsorption values were obtained by equilibrating soils with 0.01M  $\text{CaCl}_2$  containing from 0 to 12,500  $\mu\text{g}$  of P as  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ . Five grams of soil were equilibrated with 50 ml of solution. The soil suspensions were shaken for 24-hour periods at 19°C in order to achieve equilibrium. Samples were centrifuged and aliquots of supernatants were analyzed for phosphorus.

The Langmuir adsorption isotherm as discussed earlier was used to determine the adsorption maxima. It can be described by the equation  $X = \frac{KCX_m}{1+KC}$ , where K is a constant relating to the adsorption energy, C is the equilibrium P concentration, and X and  $X_m$  are phosphorus adsorbed and maximum phosphorus adsorption per unit weight of soil, respectively. The equation may be written in the linear form,

$$\frac{C}{X} = \frac{C}{X_m} + \frac{1}{KX_m} \quad (10)$$



TABLE 2  
 SELECTED CHARACTERISTICS OF SOILS USED IN PHOSPHORUS  
 ADSORPTION STUDIES

Soil Series	pH	Organic Matter	Double Acid Extractable		
			Al	Fe	P
		%	- - - - $\mu\text{g/g soil}$ - - - -		
Myakka fine sand	4.4	6.3	47	14	1.9
Felda ponded	4.8	12.6	147	45	3.2
Pompano fine sand	4.5	9.7	484	260	1.1
Samsula muck	4.4	67.2	1220	50	2.5
Basinger fine sand	4.3	18.4	324	100	2.4
Placid fine sand	5.2	40.3	97	5	0.7

and a plot of  $C/X$  against  $C$  should give a straight line of slope  $1/X_m$ , from which  $X_m$  may be calculated and the constant  $K$  obtained from the intercept.

2. Effect of aerobic and anaerobic conditions on phosphorus adsorption. Five grams of air-dried soil from the soil samples used in the previous experiment were placed on 100 ml centrifuge tubes. One set of samples was brought to approximately field capacity with deionized water and incubated under aerobic conditions. Another set was saturated with deionized water. This set of tubes was capped tightly with rubber septums and purged with  $N_2$  gas to maintain anaerobic conditions. All tubes were reincubated for 2 weeks at  $23 \pm 2^\circ C$ . After preincubation, 50 ml of phosphorus solutions (soil:solution ratio of 1:10) ranging from 0 to 250  $\mu g$  P/ml as  $Ca (H_2PO_4)_2$  were added to each sample. For the samples under anaerobic conditions, phosphorus solutions were added using a 50 ml syringe and tubes purged again with  $N_2$  gas for about 30 minutes to insure  $O_2$ -free conditions. All samples were shaken for 24 hours. Soil suspensions were centrifuged and an aliquot of supernatant was analyzed for phosphorus, iron, aluminum, and manganese.

3. Phosphorus removal from overlying water in soil-water columns. This study was conducted to determine the rate of phosphorus removal from overlying water. The same column set-up in the previous nitrification study were used in this study. Application of 5 ml of 0.20 mg P/ml  $KH_2PO_4$  solution was made to the overlying water of each column, so that the concentration of phosphorus in the water would be 2.0  $\mu g$  P/ml. The overlying water from each column was sampled periodically and analyzed for orthophosphate using the ascorbic acid procedure (Murphy and Riley, 1962). Soluble orthophosphate was also measured in KCl

extracts of soil sections taken for ammonium and nitrate analysis as noted previously. A portion of the dried soil sample used in total nitrogen analysis was extracted with double acid extractant (0.05 N HCL and 0.025 N H<sub>2</sub>SO<sub>4</sub>) and analyzed for phosphorus.

### C. Nutrient Availability from Decaying Vegetation

1. Decomposition in soil-water systems. Soil samples used in this study were collected on September 29, 1980 from the Armstrong experimental site (Figure 6). Selected soil characteristics are shown in Table 3. Simulated soil-water systems were established in approximately 1 liter glass containers using the above soil samples and distilled water. Prior to use, soil was passed through a 0.5 X 0.5 cm screen to remove roots. Two hundred grams (wet weight) of Basinger and Placid soils, and 275 gm of the Sammula muck were placed in the containers to provide a soil depth of about 4 cm. Then 600 ml of deionized water was added to each container to give about 7 cm of overlying water. The containers were left undisturbed for about 1 week for equilibration. At the same time a treatment with reservoir (marsh) water (600 ml) alone, i.e., without soil was started. After equilibration, the water in one set of containers was continuously bubbled with air and another was bubbled with N<sub>2</sub> gas to create aerobic and anaerobic conditions, respectively, in the overlying water. The experimental setup for this study is illustrated in Figure 7.

A mixture of plant material from the experimental site (mainly Panicum spp., Paspalum spp., Juncus spp.) also collected on September 29, 1980, was added to the above soil-water systems. Plant samples (3 g

TABLE 3  
 SELECTED CHARACTERISTICS OF SOILS USED IN THE  
 DECOMPOSITION STUDY

Soil	pH	Organic Matter	Double-Acid Extractable					
			K	Mg	Fe	Ca	Al	P
		%	----- $\mu\text{g/g soil}$ -----					
Basinger fine sand	4.2	18	34	16	56	98	288	3.3
Placid fine sand	5.5	40	30	52	32	2800	524	2.1
Samsula muck	3.7	93	17	102	72	520	4240	1.6

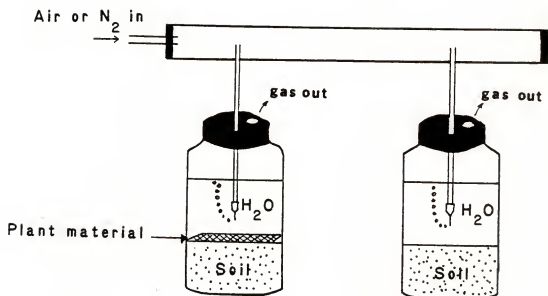


Figure 7. Schematic diagram of incubation system.

dry weight) were cut into about 2.5 cm pieces, placed in 7 X 7 cm fiber-glass screen bags, and placed in the containers. A duplicate set of soil-water systems was incubated without added plant material. All systems were incubated in the dark at 28°C for 16 weeks. After 0, 1, 2, 4, 6, 8, 12, and 16 weeks of incubation, a 40 ml water sample was taken from each jar and filtered through a 0.45  $\mu$ m filter membrane. Filtered samples were analyzed for nitrate, ammonium, orthophosphate, electrical conductivity, calcium, potassium, magnesium, pH, and dissolved oxygen. Total nitrogen and total phosphorus in filtered water were determined at the end of 0, 2, 4, 6, 8, 12 and 16 weeks on filtered water. At the end of 16 weeks, the bags containing plant material were removed, and gently washed free of sediment. The plant material was dried at 70°C for 1 week, ground, and analyzed for total carbon, nitrogen, and phosphorus.

### III. Analytical Methods

#### A. Soil Analyses

Soil samples were extracted with the double acid extractant (0.05N HCl and 0.025N H<sub>2</sub>SO<sub>4</sub>) (Mehlich, 1953) and analyzed for phosphorus using the ascorbic acid method (Murphy and Riley, 1962) and calcium, magnesium, aluminum, iron and potassium by atomic absorption spectrometry. Nitrate and ammonium were analyzed by extracting the soil with 1N KCl extractant followed by steam distillation (Bremner, 1965b). Total Kjeldahl nitrate in the soil samples was analyzed by digestion and steam distillation (Bremner, 1965a). Organic matter in the soil was determined by the Walkley-Black method (Allison, 1965).

Fresh, moist soil samples were used for pH determinations. Measurements were made in deionized water with a soil:liquid ratio of 1:1 (V:V) using a combination pH electrode and Orion 701 A meter. Redox potential of soil systems in the denitrification experiment was measured by using a platinum electrode and Orion 701 A meter.

#### B. Water Analyses

Ammonium and nitrate in the overlying water of the soil-water columns were determined by steam distillation (Bremner, 1965b). In the decomposition study, the overlying water was analyzed for ammonium and nitrate by using the following AutoAnalyzer method:

Ammonium--automated phenate method (EPA, 1979).

Nitrate--modified cadmium reduction method (EPA, 1979)  
using zinc instead of cadmium (J. De Vore, IFAS Soil  
Analytical Laboratory, personal communication).

Orthophosphate was determined by ascorbic acid method (Murphy and Riley, 1962). Total phosphorus in the water samples was determined by persulfate digestion followed by the ascorbic acid reduction method (EPA, 1979). Total Kjeldahl nitrogen was analyzed by digestion and steam distillation (Bremner, 1965a). Calcium, magnesium and potassium were determined by using atomic absorption methods. Soluble organic carbon in the water was analyzed by using direct injection module of Carbon Analyzer Model 524 B by Oceanography International Corporation. Conductivity and dissolved oxygen of the water samples were measured with a Hach Mini Conductivity meter and a YSI model 54 Oxygen Meter, respectively. The combination pH electrode and Orion 701 A meter were used for the determination of water pH.

### C. Plant Analyses

Total nitrogen in ground plant material was determined by digestion followed by steam distillation (Bremner, 1965a). Total phosphorus was estimated by ashing (first at 230°C for 1 hour and then at 450°C overnight) and digesting with concentrated nitric acid and 5N hydrochloric acid, followed by an ascorbic acid method (Murphy and Riley, 1962). Total carbon was determined by ashing (weight loss after ashing at 500°C).

### D. $^{15}\text{N}$ Analyses

Total Kjeldahl nitrogen (TKN), nitrate, and ammonium containing  $^{15}\text{N}$  in the soils or overlying water were determined by methods described previously. The titrated samples were acidified with 2 ml of 1/12N  $\text{H}_2\text{SO}_4$  and then evaporated on a hot plate so that the final solution contained approximately 1 mg N/2 ml.

The  $^{15}\text{N}$  analysis was conducted on a Micro Mass 602 mass spectrometer. Ammonium in the sample was oxidized to nitrogen gas with sodium hypobromite (Bremner, 1965c).



## CHAPTER IV

### RESULTS AND DISCUSSION

#### I. Denitrification Potential of Soils

To evaluate the nitrogen removal potential of soils in the retention/detention area, two laboratory experiments were conducted. The first experiment evaluated denitrification rates in the soil matrix in the absence of overlying water. The second experiment evaluated the effect of overlying water on both nitrification and denitrification processes which are primarily responsible for the final nitrogen loss from wetland ecosystems.

#### A. Denitrification in the Absence of Overlying Water

This experiment was conducted using the three soils from the Armstrong experimental site, namely Basinger, Placid, and Samsula soils to ascertain their capacities to reduce nitrate. Nitrate was added directly to the soil matrix and samples were incubated anaerobically up to 6 days. Nitrate concentration was measured periodically during the incubation period. Initial nitrate concentrations were 103.3, 110.3, and 92.0  $\mu\text{g N/g soil}$  in the Basinger, Placid, and Samsula soils, respectively (Figure 8). The most rapid decrease in nitrate concentration was in the Samsula soil system with a greater than 90% decrease within 2 days. In the Basinger and Placid soil systems, 6 days were

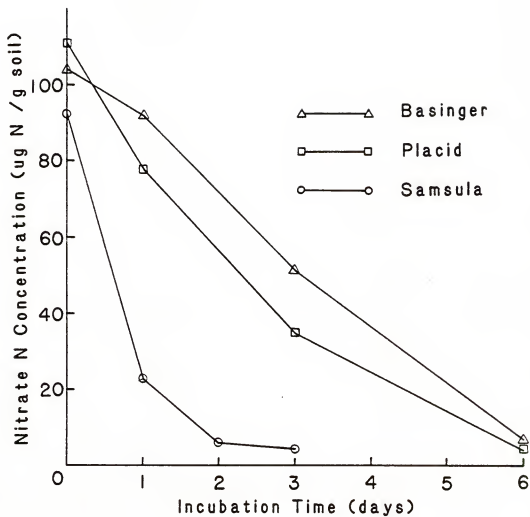


Figure 8. Nitrate disappearance rates in soils incubated under anaerobic conditions.

required to remove approximately the same amount of nitrate. When reservoir water was amended with nitrate and incubated anaerobically, only small amounts of nitrate (about 2%) were lost indicating very little (if any) denitrification in the absence of soil (data not shown). This is in agreement with the work of Engler et al. (1976) and Erickson (1978) and probably was due to the lack of readily available organic carbon.

Redox potential values of each system are shown in Table 4. The most reduced condition was found in the Samsula muck system as expected. The redox potential in this system decreased from 404 mv at the beginning of incubation to 65 mv at the end of the 3 day incubation period. Reddy et al. (1980b) observed the redox potential of organic soil used in their denitrification studies decreased from 452 mv to -252 mv at the end of 8 days incubation. They attributed the decrease in redox potential to a high demand of electron acceptors by micro-organisms in the soils. The rate of nitrate disappearance (Figure 8) increased with increasing organic matter content. The fastest rate of nitrate disappearance occurred in the Samsula soil which contains 94% organic matter and the slowest rate of nitrate disappearance was observed in the Basinger soil with 8.8% organic matter (Table 1). Along with the data for the reservoir water, these results indicate the importance of readily available carbon to the rate of nitrogen removal in these systems.

At each sampling date, soils were extracted with 1N KCl and filtered through a 0.45  $\mu$ m filter to separate exchangeable and soluble forms of nitrogen from soil TKN (Table 5). In all cases, ammonium and soluble organic levels increased with time while soil TKN did not show

TABLE 4

REDOX POTENTIAL VALUES OF THE SYSTEMS MEASURED DURING  
THE INCUBATION PERIOD

System	Incubation Period (days)				
	0	1	2	3	6
	- - - - - mv - - - - -				
Basinger	510	416		377	338
Placid	465	413		376	259
Samsula	404	331	183	65	
Reservoir Water	444	316		259	274

TABLE 5

AMOUNT OF NITROGEN IN DIFFERENT FRACTIONS OF SOILS AND RESERVOIR WATER AND DISTRIBUTION OF LABELED NITROGEN IN THE SOILS AND RESERVOIR WATER AFTER THE ADDITION OF 800  $\mu\text{g}$  N TO 8 g OF SOIL OR 800  $\mu\text{g}$  N TO 8 ml OF RESERVOIR WATER. NITROGEN ADDED TO THE LAST SET OF SAMPLES WAS LABELED WITH  $^{15}\text{N}$

Sample	Incubation Period	Soluble & Exchangeable				Soil TKN*	Soluble & Exchangeable				Soil TKN*	Total Recovery	Unaccounted for N	
		$\text{NH}_4^+$	$\text{NO}_3^-$	ON			$\text{NH}_4^+$	$\text{NO}_3^-$	ON					
days ----- $\mu\text{g}$ N in 8 g soil ----- % of added N -----														
Basinger	0	3.0	825.6	39.8	10,400									
	1	21.0	735.8	51.1	12,800									
	3	56.8	412.8	240.5	14,400									
	6	65.8	56.8	378.4	18,400	1.2	1.6	0.2	0.01	3.0			97.0	
Placid	0	34.6	882.5	83.9	29,600									
	1	34.6	623.1	102.8	25,600									
	3	63.0	283.2	348.1	30,400									
	6	88.0	37.8	363.3	24,000	1.0	-	0.1	-	1.0			98.9	
Samsula	0	59.1	736.3	340.8	91,200									
	1	117.3	182.9	317.0	92,000									
	2	126.6	46.9	554.8	102,400									
	3	229.8	32.8	416.1	125,600	2.8	-	0.5	0.8	4.1			95.9	

Continued

TABLE 5

CONTINUED

Sample	Incubation Period	Soluble & Exchangeable			Soil	Soluble & Exchangeable			Soil	Total Recovery	Unaccounted for N
		$\text{NH}_4^+$	$\text{NO}_3^-$	ON	TKN*	$\text{NH}_4^+$	$\text{NO}_3^-$	ON	TKN*		
----- µg N in 8 ml ----- % of added N -----											
Reservoir water	0	14.3	688.6	28.5							
	1	4.8	664.7	32.8							
	3	19.1	602.5	18.5							
	6	9.5	675.0	49.8		-	83.5	2.0		85.5	14.5

\* Does not include soluble and exchangeable NH<sub>4</sub><sup>+</sup> and organic N.

any definite trends. The increases in ammonium and soluble nitrogen appear to be coming from original soil organic matter and not added nitrate. Very little labeled nitrogen was found in these fractions at the end of the study. The largest amount of nitrate which was reduced to ammonium or immobilized into organic nitrogen (2.8 and 1.3% of added labeled nitrate, respectively) was found in the Samsula soil system. The high organic matter content of this soil, which can serve as a carbon source for microorganisms, probably enhanced the immobilization process which incorporated ammonium and/or nitrate into microbial biomass. These observed amounts of nitrate reduced and immobilized are comparable to values found by Reddy et al. (1980b) in a water-saturated organic soil system. They reported that 2.5 and 0.6% of added labeled nitrate was reduced to ammonium and immobilized into organic nitrogen, respectively. In the Placid soil systems, 1% of added labeled nitrate was reduced to ammonium and 0.1% was immobilized and released as soluble organic nitrate. Similar results were obtained for the Basinger soil system. In the reservoir water system, the nitrate, ammonium, and total organic nitrogen concentrations did not show any definite trends during the incubation period. A small amount of nitrate was lost during the incubation period, with about 83.5% of the added labeled nitrate remaining in the system. None of the labeled nitrogen was detected in the ammonium fraction and only 2% was in organic nitrogen.

The major portion of labeled nitrogen was unaccounted for, i.e. 97.0, 98.9, and 95.9% in the Basinger, Placid, and Samsula soil systems, respectively. A considerably lower amount of labeled nitrogen (14.5% of added labeled nitrate) was unaccounted for in the reservoir water system.

Unaccounted-for labeled nitrogen can best be attributed to loss by denitrification since ammonium volatilization is very unlikely in these low pH systems.

In an attempt to evaluate the kinetics of denitrification in these systems, it was found that denitrification appeared to follow zero-order kinetics in the Basinger soil system, i.e. the plot of nitrate concentration vs time gives an almost straight line with  $r^2 = 0.995$ . The denitrification rate in the Basinger soil system was  $16.44 \mu\text{g N/g soil/day}$ . In a recent study, Reddy et al. (1978) also found nitrate reduction in mineral soils followed zero-order kinetics when carbon was nonlimiting, which was due to the fact that the nitrate was in direct contact with the active denitrification sites in soil. In the Placid and Samsula soil systems, denitrification rate was better described by first-order kinetics.

A first-order rate equation can be described as follows:

$$\ln \frac{[\text{NO}_3^-\text{N}]_t}{[\text{NO}_3^-\text{N}]_0} = -kt \quad (10)$$

where  $[\text{NO}_3^-\text{N}]_t$  = nitrate concentration in soil or overlying water at time  $t$ ,  $\mu\text{g N/g soil}$  or  $\mu\text{g N/ml}$

$[\text{NO}_3^-\text{N}]_0$  = initial nitrate concentration,  $\mu\text{g N/g soil}$  or  $\mu\text{g N/ml}$

$k$  = first-order rate constant,  $\text{day}^{-1}$

$t$  = time, days.

By fitting nitrate disappearance data into Equation 10, first-order rate constants ( $k$ ) of  $0.528 \text{ day}^{-1}$  ( $r^2=0.978$ ) and  $1.070 \text{ day}^{-1}$  ( $r^2=0.948$ ) were obtained for the Placid and Samsula soil systems, respectively.



These observed first-order kinetic characteristics of denitrification are probably controlled by the diffusion of nitrate within the soil-water to the enzymatic sites. Diffusion of nitrate becomes more important in determining denitrification rate when large amounts of water are present in soil pores (Reddy et al., 1980). Large volumes of water-filled pores were observed in the Samsula and Placid soils, likely due to their organic matter content. Reddy et al. (1980b) also reported that nitrate reduction rates in organic soil with no excess flood water were best described by first-order kinetics with an average rate constant ( $k$ ) of  $0.757 \text{ day}^{-1}$ .

#### B. Nitrification and Denitrification in Soil-Water Columns

Nitrification. Nitrification is an important process because ammonium must be converted to nitrate before it can be denitrified. Since nitrification is inhibited by low pH, particularly lower than 5, the nitrification rate in the soils of the Armstrong site might be significantly affected by low pH (see Table 1). This experiment was conducted to evaluate the nitrification rate which might be expected in the retention/detention area. Overlying water (reservoir water) in soil-water columns was amended with  $^{15}\text{N}$  labeled ammonium sulfate to obtain an initial concentration of about  $23 \mu\text{g N/ml}$ . Ammonium and nitrate levels were then determined over a 25 day period.

Concentrations of ammonium and nitrate in the overlying water are summarized in Table 6 and depicted graphically in Figures 9 and 10. Ammonium in the overlying water decreased with time in all systems with the fastest decrease observed in the Samsula soil-water columns. The reductions of ammonium concentration in the Placid and Basinger soils were

TABLE 6

AMMONIUM, NITRATE, DISSOLVED OXYGEN, AND pH VALUES  
MEASURED IN THE OVERLYING WATER OF SOIL-WATER  
COLUMNS CONTAINING ADDED 12.5 mg N AS AMMONIUM  
SULFATE, INCUBATED FOR 25 DAYS

Treatment	Days					
	0	2	5	10	15	25
----- $\text{NH}_4^+$ -N, $\mu\text{g N/ml}$ -----						
Control, Basinger	0.2	0.1	0.2	<0.1	<0.1	<0.1
Control, Placid	0.3	<0.1	<0.1	<0.1	0.2	0.4
Control, Samsula	0.7	0.6	0.1	0.2	0.2	<0.1
-----						
Treated Basinger	23.0	21.1	19.8	18.5	17.3	16.6
Treated Placid	23.6	21.4	19.5	17.7	16.7	15.8
Treated Samsula	23.5	20.3	16.8	11.4	8.6	6.1
----- $\text{NO}_3^-$ , $\mu\text{g N/ml}$ -----						
Control, Basinger	0.3	0.1	0.1	0.1	<0.1	<0.1
Control, Placid	0.1	0.6	0.1	<0.1	0.1	0.1
Control, Samsula	0.1	0.7	0.6	0.3	0.1	0.1
-----						
Treated Basinger	0.7	0.8	1.1	1.7	1.8	0.6
Treated Placid	0.8	0.8	1.5	1.4	1.3	0.2
Treated Samsula	0.7	1.2	2.5	3.4	2.7	0.6
----- Dissolved oxygen, ppm -----						
Control, Basinger	7.2	7.6	7.4	7.7	7.2	7.4
Treated Basinger	7.4	7.7	7.5	7.4	7.3	7.4
Control, Placid	7.3	7.6	7.2	7.6	7.4	7.4
Treated Placid	7.0	7.7	7.5	7.4	7.4	7.3
Control, Samsula	7.2	7.5	7.2	7.7	7.3	7.1
Treated Samsula	7.3	7.7	7.4	7.5	7.3	7.4

Continued

TABLE 6  
CONTINUED

Treatment	Days					
	0	2	5	10	15	25
	pH					
Control, Basinger	5.6	5.4	5.5	6.1	6.2	5.4
Control, Placid	5.2	4.8	4.5	5.3	4.4	4.2
Control, Samsula	6.9	6.8	6.7	7.0	7.1	7.0
Treated Basinger	5.3	5.0	4.8	5.3	5.1	4.9
Treated Placid	5.6	5.4	4.8	5.3	4.9	4.6
Treated Samsula	6.6	6.7	5.7	5.7	5.3	5.3

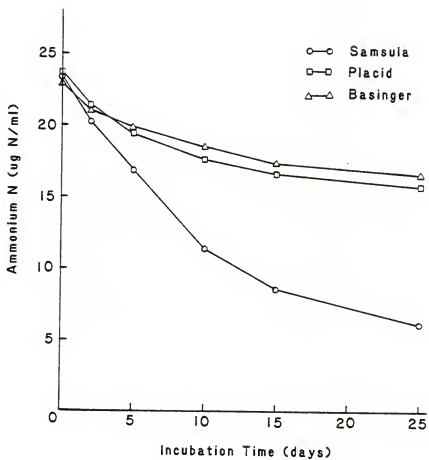


Figure 9. Ammonium disappearance rates in the overlying water of the soil-water columns.

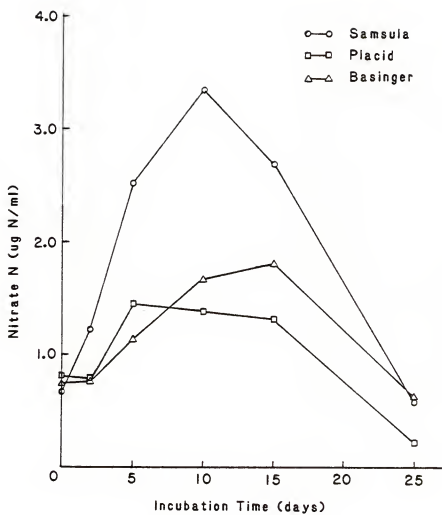


Figure 10. Nitrate accumulation in the overlying water of the soil-water columns.

approximately equal and much less than in the Samsula soil-water columns. After 25 days of incubation, 26, 67, and 72% of the initial ammonium remained in the Samsula, Placid, and Basinger soil-water columns, respectively. Labeled ammonium (Table 7) also shows a decrease in concentration in the overlying water. However, the labeled nitrogen as ammonium remaining in the overlying water after 25 days of incubation was lower than the total ammonium with 16, 37, and 57% of added labeled ammonium in the Samsula, Placid, and Basinger soil-water columns, respectively. Higher amounts of total ammonium in the overlying water was probably due to the release of ammonium from soil organic nitrogen through mineralization. These results indicate that the pH of the overlying water (Table 6) which was directly related to soil pH (Table 1), appeared to be the controlling factor affecting nitrification in these systems.

The loss of ammonium in the overlying water can be due to immobilization, nitrification, fixation to the sediment, and ammonia volatilization. The latter is very unlikely due to low pH in the soil-water systems. There are evidences for nitrification such as the decrease in pH of the overlying water (Table 6) due to release of hydrogen ions by the nitrification process. For the Samsula soil-water columns, pH of the overlying water decreased from 6.6 at the beginning of the incubation to 5.3 at the end of the incubation. The pH of the overlying water in Placid and Basinger systems fluctuated somewhat during the incubation but still showed a decreasing trend. After 5 days of incubation, the pH of the overlying water in the Placid and Basinger systems decreased to 4.8 which appeared to affect nitrification as indicated by the leveling off of the ammonium removal curves (Figure 9). Nitrifying bacteria

TABLE 7

NITROGEN RECOVERY AS AMMONIUM IN THE OVERLYING WATER DURING  
THE 25 DAY INCUBATION PERIOD PRESENTED AS  
PERCENT OF ADDED LABELED AMMONIUM

Underlying Soil	Recovery of Added Labeled Ammonium					
	Days of Incubation					
	0	2	5	10	15	25
	- - - - - % - - - - -					
Basinger	91.0	83.1	75.0	62.1	59.9	56.8
Placid	94.1	80.2	74.6	64.9	58.0	37.1
Samsula	90.0	75.6	60.0	31.4	25.2	16.0

require a pH around 7 or higher to do well and are considerably inhibited by pH values below 5.

Nitrification was also evidenced by the accumulation of nitrate in the overlying water (Figure 10, Table 6). The highest nitrate level of 3.37  $\mu\text{g N/ml}$  was observed in the Samsula system, while 1.45 and 1.81  $\mu\text{g N/ml}$  were the maximum concentrations of nitrate in the Placid and Basinger systems, respectively. All nitrate levels in these systems decreased with time after reaching their peak values. Nitrate levels never reached levels equivalent to ammonium disappearance. This may be attributed to immobilization, ammonium fixation, and concurrent nitrification-denitrification reactions occurring in these systems. The latter is typical of soil-water systems underlain by anaerobic soil (Patrick and Reddy, 1976). The extent of denitrification in these systems was further evaluated and will be discussed in the next section.

After 25 days of incubation, the overlying water was removed from the columns. The soil cores were sectioned and analyzed for KCl extractable (soluble and exchangeable) ammonium, nitrate, and TKN. These nitrogen fractions were also analyzed for  $^{15}\text{N}$ . The concentrations of soluble and exchangeable ammonium and nitrate in the Basinger, Placid, and Samsula soil columns are shown in Figures 11 to 13. About a three-fold increase in ammonium concentration was observed in the soil when ammonium was added to the overlying water (Figures 11B to 13B) as compared to the control columns (Figures 11A to 13A). These data indicated that some of the ammonium from the overlying water was adsorbed by soils. The amount of adsorbed ammonium varied slightly among soil types. Ammonium adsorption as indicated by  $^{15}\text{N}$  ranged from 5.7 to 3.3% of added labeled ammonium (Table 8).



## Basinger

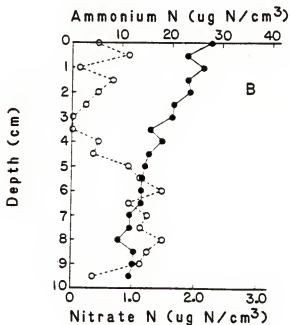
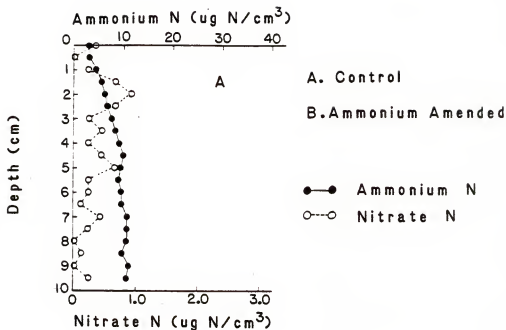


Figure 11. Distribution of ammonium and nitrate in the Basinger soil columns.

## Placid

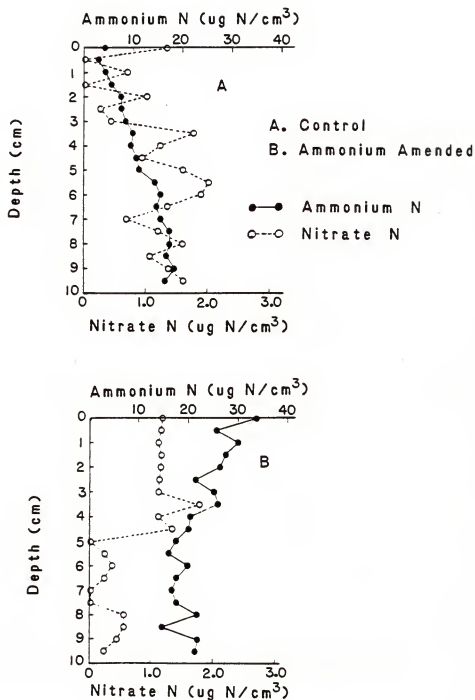


Figure 12. Distribution of ammonium and nitrate in the Placid soil columns.

## Samsula

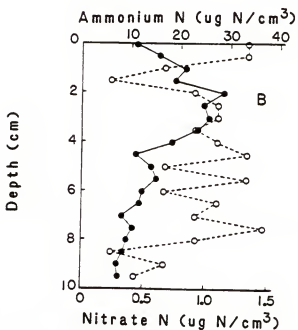
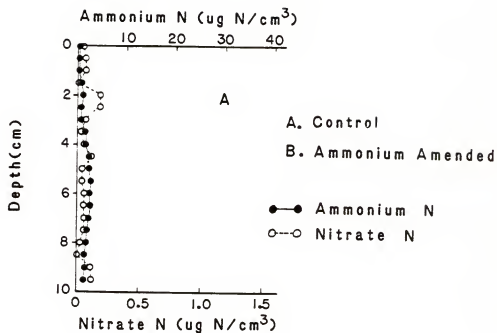


Figure 13. Distribution of ammonium and nitrate in the Samsula soil columns.

TABLE 8

DISTRIBUTION OF LABELED NITROGEN IN THE OVERLYING WATER AND UNDERLYING SOIL ON 25th DAY AFTER THE ADDITION OF 12,500  $\mu\text{g}$  N AS LABELED AMMONIUM SULFATE TO THE OVERLYING WATER AT THE BEGINNING OF NITRIFICATION STUDY

Soil-Water System	<u>Recovery of Added Labeled Ammonium</u>			Total Recovery	Unaccounted- for N
	<u>Overlying Water</u>	<u>Soil</u>			
	$\text{NH}_4^+$	Soluble & Exch.	TKN		
	$\text{NH}_4^+$				

Recovery of  $^{15}\text{N}$  in different nitrogen fractions at the end of the study is shown in Table 8. A considerable amount of the added nitrogen (56.8, and 37.1%) remained in ammonium form in the overlying water of the Basinger and Placid soil-water columns, respectively. Only 16% remained in ammonium form in the overlying water of the Samsula system. Some immobilization of added ammonium was observed as evidenced by the recovery of 4.9 to 11.8% of added  $^{15}\text{N}$  in the soil TKN fraction. Ammonium immobilization was greatest in the Samsula system and lowest in the Basinger system, probably due to higher available carbon in the Samsula soil. On the average, about 50% of the added  $^{15}\text{N}$  was not accounted for at the end of the study.

Some of the unaccounted-for nitrogen could have been present in (1) the overlying water as nitrate which was at an insufficient level for  $^{15}\text{N}$  analysis or (2) the underlying soil as soluble nitrate which was also at an insufficient level for  $^{15}\text{N}$  analysis. However, the total quantity of these 2 fractions at the end of the incubation was only about 2% of the 12,500  $\mu\text{g}$  added nitrogen. Some of the unaccounted-for nitrogen could also have been present as soluble organic nitrogen in the overlying water. This fraction was not measured; however, it is not likely to be a significant amount. Therefore, most of the unaccounted-for nitrogen was very likely lost by nitrification-denitrification reactions. Ammonium was likely oxidized to nitrate in the aerobic zone of the soil-water system and then the nitrate diffused into the anaerobic layer of the underlying soil where it was denitrified to nitrogen gas. Other workers (Reddy and Graetz, 1981; Reddy et al., 1980b; Tusneem and Patrick, 1971; Buresh, 1978) have reported similar loss of added labeled ammonium in soil-water systems.

The results obtained in this study on rates of ammonium removal in the three soil-water systems are presented in Table 9. Ammonium removal

TABLE 9  
AMMONIUM REMOVAL RATES IN THE THREE SOIL-WATER SYSTEMS

Soil Type	Zero-Order Kinetic			First-Order Kinetic		
	Ammonium Removal Rate					
	Calculated from*	r <sup>2</sup> *	Calculated from*** Labeled NH <sub>4</sub> <sup>+</sup> -N	Rate Constant* Calculated from Total NH <sub>4</sub> <sup>+</sup> -N	Calculated from Total NH <sub>4</sub> <sup>+</sup> -N	r <sup>2</sup> **
	μgN/ml/day		μgN/ml/day	day <sup>-1</sup>		
Basinger	0.24	0.86	0.31	0.012		0.89
Placid	0.29	0.83	0.46	0.014		0.90
Samsula	0.69	0.90	0.63	0.055		0.97

\* Calculated from the decrease in NH<sub>4</sub><sup>+</sup>-N concentration.

\*\* Number of observations for each soil = 6.

\*\*\* Calculated from the unaccounted for labeled nitrogen over a 25 day period.

rates were calculated by two methods, i.e., (1) based on the decrease in total ammonium concentration and (2) labeled ammonium which cannot be accounted for over the 25 day period. The rate of nitrification calculated by total ammonium can be described by a linear regression analysis, indicating that nitrification followed zero-order kinetics which is independent of the ammonium concentration in the systems. The ammonium removal rates calculated based on the total ammonium were 0.24, 0.29, and 0.69  $\mu\text{g N/ml/day}$  for the Basinger, Placid, and Samsula systems, respectively. Using the unaccounted for labeled nitrogen, the rates of ammonium removal were 0.31, 0.46, 0.63  $\mu\text{g N/ml/day}$  for the Basinger, Placid, and Samsula systems, respectively. The slightly lower rates of nitrification in the Basinger and Placid systems calculated based on total ammonium might have been due to some small amount of unlabeled ammonium released from the organic fractions to the overlying water through the mineralization process. Several workers observed nitrification to be independent of ammonium concentration (Anderson, 1965; Reddy et al., 1980b; Wild et al., 1971). Reddy et al. (1980b) reported that nitrification in the aerobic soil layer of flooded soil followed zero-order kinetics and nitrification rates ranged from 1.2 to 3.5  $\mu\text{g/g/day}$  in different soils.

An attempt was made to fit nitrification data (the decrease in ammonium concentration) into the first-order kinetic equation, whereby the rate constants ( $k$ ) were calculated (Table 9). The first-order rate constants ( $k$ ) calculated for ammonium removal in the Basinger, Placid, and Samsula systems were 0.012, 0.014, and 0.055  $\text{day}^{-1}$ , respectively. The  $r^2$  values obtained in these calculations (Table 9) indicate that

ammonium removal in these systems conformed better to the first-order than zero-order kinetics. These results can be explained by the fact that pH is one of the major factors controlling the activity of nitrifiers. Even though nitrification rates are independent of ammonium concentration, they can also be highly affected by the gradual reduction of pH in the systems as discussed earlier.

Denitrification. Additional laboratory studies were conducted to evaluate further the extent of denitrification in the soil-water columns. Addition of nitrate to the overlying water simulated nitrate input to the wetland soil from agricultural drainage water. The overlying water in each column was amended with  $^{15}\text{N}$ -labeled nitrate so that the initial nitrate concentration in the overlying water was approximately 23  $\mu\text{g N/ml}$ .

Concentrations of nitrate, ammonium, dissolved oxygen, and pH over a 25 day period in the overlying water of the three soil-water systems are summarized in Table 10. Nitrate disappearance data are depicted graphically in Figures 14A and 14B. The most rapid decrease in nitrate concentration was observed in the Samsula soil-water column, with only 28% of initial nitrate remaining in the overlying water at the end of 25 days compared to 41 and 62% for the Placid and Basinger soil-water columns, respectively. These data suggest that soil pH and organic matter content (Table 1) were directly related to denitrification rate, but the extent of denitrification in these systems was not as great as in the preceeding denitrification study where nitrate was added directly to the soil matrix. This can be explained by the fact that nitrate in the overlying water must diffuse downward



TABLE 10

NITRATE, AMMONIUM, DISSOLVED OXYGEN, AND pH VALUES  
MEASURED IN THE OVERLYING WATER OF SOIL-WATER  
COLUMNS WITH ADDITION OF 12.5 mg N AS POTAS-  
SIUM NITRATE, AND INCUBATED FOR 25 DAYS

Soil-Water System*	Days					
	0	2	5	10	15	25
----- $\text{NO}_3^-$ -N, $\mu\text{g N/ml}$ -----						
Basinger	22.4	21.1	20.2	18.2	16.9	13.9
Placid	23.2	21.9	19.7	17.4	14.8	9.6
Samsula	22.5	19.6	17.9	13.9	11.3	6.3
----- $\text{NH}_4^+$ , $\mu\text{g N/ml}$ -----						
Basinger	0.8	0.8	0.9	1.7	1.0	0.3
Placid	0.6	0.5	0.7	1.6	1.8	1.4
Samsula	1.0	1.1	0.8	1.0	2.0	0.4
----- Dissolved Oxygen, ppm -----						
Basinger	7.5	7.8	7.4	7.5	7.3	7.4
Placid	7.7	7.7	7.5	7.4	7.4	7.4
Samsula	7.8	7.6	7.4	7.4	7.3	7.2
----- pH -----						
Basinger	5.3	5.1	5.1	6.2	6.0	5.6
Placid	4.9	4.7	4.7	5.9	5.9	5.8
Samsula	6.5	6.6	6.7	7.0	7.4	7.4

\*Values for the control (without added potassium nitrate) are the same as those noted in Table .

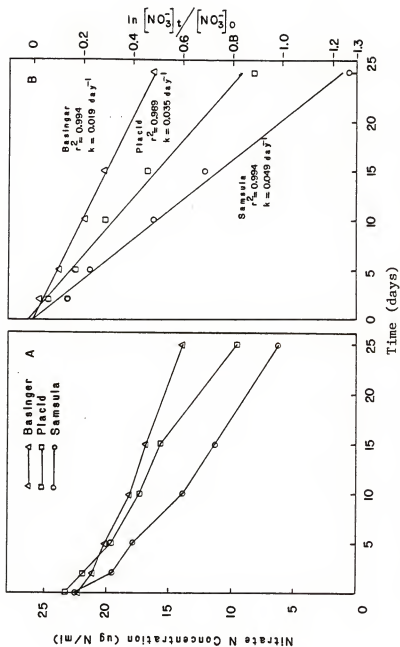


Figure 14(A) and (B). Nitrate disappearance rates in the soil-water columns with addition of nitrate to the overlying water.

to the anaerobic soil layer to be denitrified. Therefore, nitrate diffusion rate has an effect on the overall denitrification rate. Reddy et al. (1978) also showed that in soil-water systems, diffusion of nitrate from the floodwater layer into the underlying soil limited the supply of nitrate to the soil, thereby slowing the denitrification rate. It should be remembered that these soil-water columns were exposed to the air plus the upper portion of the overlying water was continuously aerated. Therefore, all denitrification in the soil-water column had to occur in the anaerobic soil layer.

Denitrification in systems with overlying water is generally considered to follow first-order kinetics (Reddy et al., 1978; 1980b; Krottje, 1980). Denitrification in all three soil-water systems also was best described by the first-order kinetic equation (Figure 14B). The calculated nitrate disappearance rate constants based on total nitrate were 0.019, 0.035, and 0.049  $\text{day}^{-1}$  for the Basinger, Placid, and Samsula soil-water systems, respectively. Denitrification rates were also calculated based on the decrease in labeled nitrate (Table 11) in the overlying water. Using labeled nitrate, the denitrification rate constants were 0.020, 0.037, and 0.062  $\text{day}^{-1}$  for the Basinger, Placid, and Samsula soil-water systems, respectively. The values for the denitrification rate constants using the two methods as described above were very close, except for the Samsula system. Denitrification rate constant for the Samsula system was lower when the calculation was based on the total nitrate than when based on the labeled nitrate. However, the difference was not great (about 0.01  $\text{day}^{-1}$  different). This was probably due to some increase in unlabeled nitrate in the overlying water due to the oxidation of ammonium.

TABLE 11

NITROGEN RECOVERY IN NITRATE FRACTION IN THE OVERLYING WATER  
FROM DENITRIFICATION STUDY DURING THE INCUBATION PERIOD OF  
25 DAYS PRESENTED AS PERCENT OF ADDED LABELED NITRATE

Soil-Water System	Recovery of Added Labeled Nitrate					
	Days of Incubation					
	0	2	5	10	15	25
	----- % -----					
Basinger	91.3	83.6	79.6	65.0	63.6	55.1
Placid	93.4	92.3	78.2	50.7	56.6	37.6
Samsula	88.3	77.1	71.1	42.2	38.8	18.4

Denitrification rate constants can also be predicted by an equation developed by Krottje (1980) based on pH and soil organic carbon content. The predicting equation is stated as follows:

$$k_1 = \sqrt{(8.9 \times 10^{-4})(OCW) - (3.9 \times 10^{-4})(OCW)(pH_{6.5}) + 0.002} \quad (12)$$

where  $k_1$  is apparent first-order denitrification rate constant,  $\text{day}^{-1}$ ; OCW is organic carbon content by weight, %; and  $pH_{6.5}$  is pH-deficit below 6.5. Predicted denitrification rate constants for the three soil-water systems are compared to calculated values in Table 12. Some variations were observed between the values of observed and predicted denitrification rate constants. These variations might be due to the fact that the predicted equation does not include other factors which can affect the denitrification such as temperature and denitrifier population.

Equivalent nitrate removal rates in g/ha/day were calculated using the rate constants calculated from labeled nitrate concentrations, and assuming a nitrate concentration of 10  $\mu\text{g N/ml}$  in 15 cm of overlying water (Table 12). It was found that the Basinger soil-water system can remove nitrate at the rate of 300 g/ha/day, while 560 and 930 g/ha/day can be removed by the Placid and the Samsula soil-water systems, respectively.

At the termination of the incubation period, the overlying water was removed from the columns and the soil cores were sectioned and analyzed for KCl extractable ammonium and nitrate, and TKN in the soil after KCl extraction. These nitrogen fractions were also analyzed for  $^{15}\text{N}$ . The concentration of soluble and exchangeable ammonium and nitrate in the

TABLE 12  
DENITRIFICATION RATE CONSTANTS AS OBSERVED FROM THIS STUDY AND AS PREDICTED BY EQUATION 12

Soil Type	pH	Total Organic Carbon	Rate Constant						Equivalent*** Nitrate Removal Rate
			Observed			Predicted			
			$r^{2**}$	Calculated from* Total $\text{NO}_3$ Disappearance	$r^{2**}$	Calculated from* Labeled $\text{NO}_3$ Disappearance	$r^{2**}$		
		%	-- day <sup>-1</sup>	-- day <sup>-1</sup>	-- day <sup>-1</sup>	-- day <sup>-1</sup>	-- day <sup>-1</sup>	-- g/ha/day --	
Basinger	3.5	5.1	0.99	0.019	0.020	0.93	0.024	300	
Placid	3.8	11.7	0.99	0.035	0.037	0.91	0.010	560	
Samsula	4.7	54.5	0.99	0.049	0.062	0.98	0.111	930	

\* Calculated from the decrease in nitrate concentration in the overlying water.

\*\* Number of observations for each soil = 6.

\*\*\* Calculated from observed rate constants which calculated from labeled nitrate, assuming a nitrate concentration of 10  $\mu\text{g N/ml}$  in the 15 cm of overlying water.

Basinger, Placid, and Samsula soil columns are presented in Figure 15. In all three soil columns, nitrate concentrations, particularly at the top 2 cm, increased when the overlying water was amended with nitrate, as compared with the control columns (Figures 11A to 13A). However, this increase was quite small when compared with the total amount of nitrogen added. The total amount of nitrate extracted by KCl from the top 10 cm of the Basinger and Samsula soil columns were only about 3 and 1% of added nitrate, respectively, while less than 1% was found in the Placid soil column. This increase in nitrate was probably due to nitrate diffusion from the overlying water. Nitrate levels in the top 2 cm of the Basinger and Placid soils were relatively high at the surface and decreased continuously to a depth of 1 or 2 cm. The depth at which the nitrate levels tend to stabilize likely reflect the depth at which denitrification is occurring. The Samsula soil did not show this increase at the surface suggesting that denitrification was occurring at the sediment-water interface. The concentration of KCl extractable ammonium in the Samsula soil column increased when the overlying water was amended with nitrate, as compared to the control column. This might be due to nitrate reduction to ammonium in the underlying soil.

The recovery of labeled nitrate in the soil-water columns 25 days after the addition of nitrate is shown in Table 13. High quantities of the added nitrate, 55.1 and 37.6%, remained in the overlying water of the Basinger and Placid soil-water columns, respectively, while in the Samsula soil-water column only 18.4% remained in the overlying water. Reduction of labeled nitrate to either ammonium or organic nitrogen was very small in all three soil-water systems. This was indicated by the

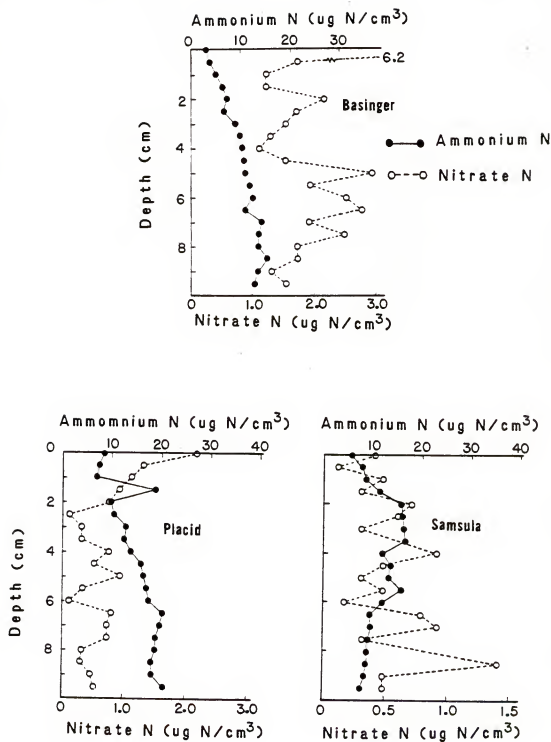


Figure 15. Distribution of ammonium and nitrate in the Basinger, Placid, and Samsula soil columns with nitrate added to the overlying water in denitrification study.



TABLE 13

DISTRIBUTION OF LABELED NITROGEN IN THE OVERLYING WATER AND UNDERLYING SOIL ON 25TH DAY AFTER ADDITION OF 12,500  $\mu\text{g}$  N AS  $^{15}\text{N}$ -LABELED POTASSIUM NITRATE TO THE OVERLYING WATER

Soil-Water System	Recovery of Added Labeled Nitrate			Total Recovery	Unaccounted for N
	Overlying Water $\text{NO}_3^-$	Soil Soluble + Exch. $\text{NH}_4^+$	TKN		
Basinger	55.1	0.2	0.5	55.8	44.2
Placid	37.6	0.4	1.7	39.7	60.3
Samsula	18.4	0.2	2.1	20.7	79.3

small amount of  $^{15}\text{N}$  recovery as soluble and exchangeable ammonium and the TKN (Table 13). The total recovery of labeled nitrate ranged from 20.7 to 55.8% with highest recovery in the Basinger soil-water system and lowest in the Samsula soil-water system.

Some of the unaccounted-for nitrogen could have been present in (1) the overlying water as ammonium which was at an insufficient level for  $^{15}\text{N}$  analysis or (2) the soil as soluble nitrate which was at an insufficient level for  $^{15}\text{N}$  analysis. However, the total amount of these 2 fractions of nitrogen at the end of the incubation was only about 5% of the 12,500  $\mu\text{g}$  added nitrogen. Some of the unaccounted-for nitrogen could also have been presented as soluble organic nitrogen in the overlying water. This fraction was not measured; however, it is not likely to be a significant amount. Ammonia volatilization is very unlikely because the pH of these systems was too low (<8) to initiate this process. Therefore, the unaccounted-for nitrogen was most likely lost from the soil-water systems due to denitrification.

## II. Phosphorus Removal Potential of Soils

To evaluate the potential of wetland soils in removing phosphorus from agricultural drainage water, three experiments were conducted. These were (1) determination of the phosphorus adsorption maxima of six air dried soils from the two experimental sites, (2) evaluation of the phosphorus adsorption characteristics of soils as affected by aerobic and anaerobic conditions, and (3) determination of the phosphorus removal rate from overlying water to the soil.

### A. Determination of Phosphorus Adsorption Maxima

Adsorption isotherms for the six soil types are shown in Figures 16A to 21A. Adsorption maxima ( $X_m$ ) were calculated from these data using

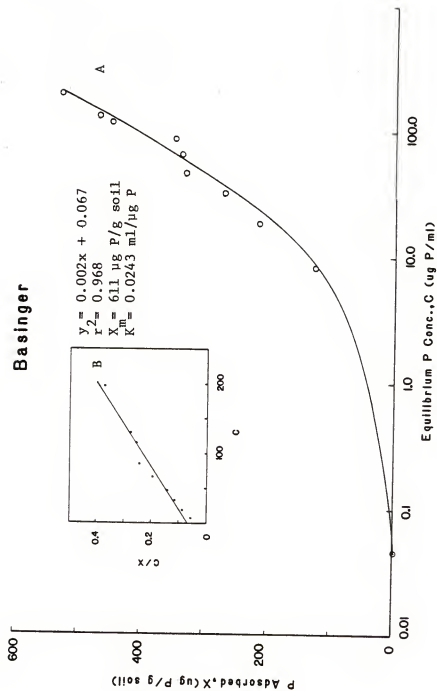


Figure 16. Adsorption of P by Basinger soil (equilibrium pH = 3.3) expressed as (A) P adsorbed vs equilibrium P conc. and (B) Langmuir plot.

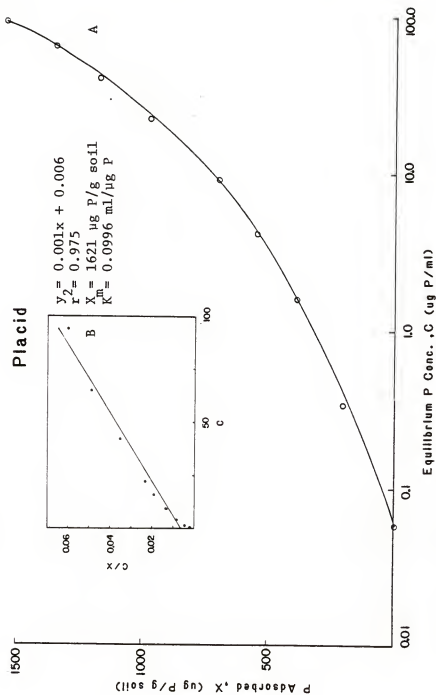


Figure 17. Adsorption of P by Placid soil (equilibrium pH = 4.5) expressed as (A) P adsorbed vs equilibrium P conc. and (B) Langmuir plot.

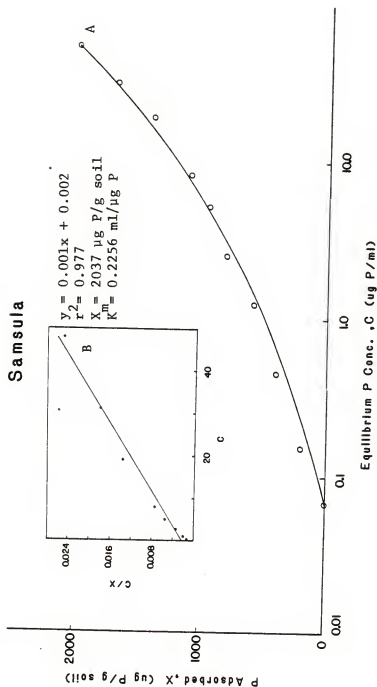


Figure 18. Adsorption of P by Samsula soil (equilibrium pH = 4.2) expressed as (A) P adsorbed vs equilibrium P conc. and (B) Langmuir plot.

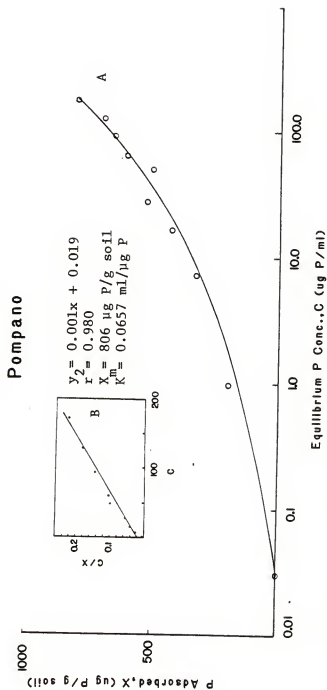


Figure 19. Adsorption of P by Pompano soil (equilibrium  $\text{pH} = 3.6$ ) expressed as (A) P adsorbed vs equilibrium P conc. and (B) Langmuir plot.

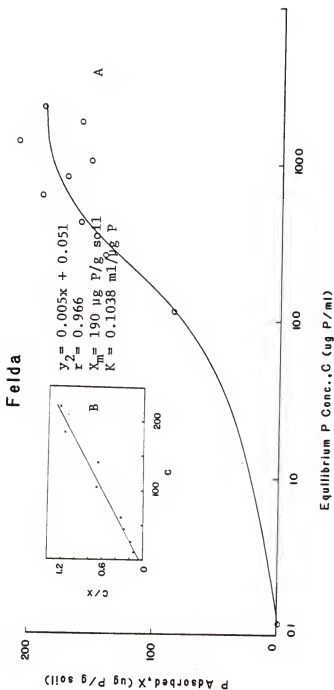


Figure 20. Adsorption of P by Felda soil (equilibrium pH = 4.2) expressed as (A) P adsorbed vs equilibrium P conc. and (B) Langmuir plot.

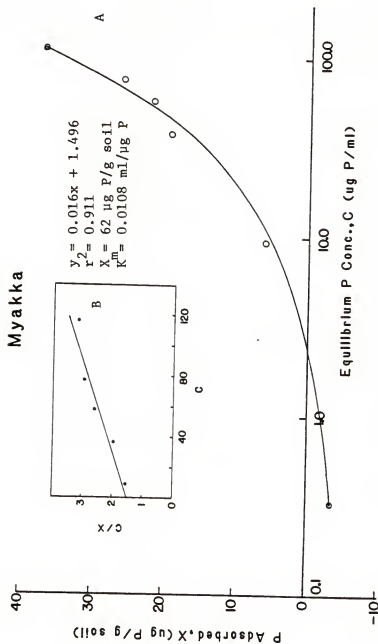


Figure 21. Adsorption of P by Myakka soil (equilibrium pH = 3.3) expressed as (A) P adsorbed vs equilibrium P conc. and (B) Langmuir plot.



the linear form of the Langmuir equation as shown in Figure 16B to 21B. Table 14 presents selected soil characteristics and summarized phosphorus adsorption data for the six soils investigated. The values of  $X_m$  for each soil indicate the capacity of a soil to retain phosphate. The highest phosphate retention capacities of 2,034 and 1,621  $\mu\text{g P/g soil}$  were found in the Samsula and the Placid soils, respectively. The Myakka and Felda soils had relatively low phosphate retention capacities (52 and 190  $\mu\text{g P/g soil}$ , respectively). Phosphorus adsorption was highly correlated with the organic matter content ( $r^2=0.87$ ) and exchangeable aluminum content ( $r^2 = 0.99$ ), excluding the phosphorus adsorption by the Placid soil. When the phosphorus adsorption value for the Placid series is included, the  $r^2$  for exchangeable aluminum content and phosphorus adsorption is reduced to 0.47. From these data it can be interpreted that phosphorus in all soil types except the Placid is being retained through an organic matter-Al- $\text{PO}_4^{-3}$  bridge. In a recent study, Bloom (1981) also illustrated that phosphorus can be retained readily through an Al-peat complex. Because of the high level of double-acid extractable calcium in the Placid soil, it is more likely that phosphorus is retained by calcium compounds in this soil. In all six soil types, extractable iron content appeared to play an insignificant role in the retention of phosphorus as indicated by a poor correlation between extractable iron and adsorption maxima ( $r^2=0.007$ ).

The calculated K values in Table 14 are constants or coefficients which are related to the bonding energy of phosphate to soil. It is still questionable about the significance of these K values in regard to phosphorus adsorption but some researchers suggested that they may be useful in describing partitioning of phosphate between solid and

TABLE 14

SELECTED CHARACTERISTICS AND PHOSPHORUS ADSORPTION DATA FOR THE SOILS INVESTIGATED

Soil Series	pH	Organic Matter %	Double-Acid Extractable				$X_m^*$	$K^{**}$
			Al	Fe	Ca	P		
			- - - - $\mu\text{g/g soil}$ - - -				$\mu\text{g P/g soil}$	ml/ $\mu\text{gP}$
Basinger fine sand	4.3	18.4	324	100	256	2.4	611	0.0243
Placid fine sand	5.2	40.3	97	5	3,920	0.7	1,621	0.0996
Samsula muck	4.4	67.2	1,220	50	530	2.5	2,037	0.2256
Pompano fine sand	4.5	9.7	484	260	672	1.1	806	0.0657
Felda ponded	4.8	12.6	147	45	1,680	3.2	190	0.1038
Nyakka find sand	4.4	6.3	47	14	320	1.9	62	0.0108

\*  $X_m$  = adsorption maximum.\*\*  $K$  = constant relating to the adsorption energy in the Langmuir equation.

solution phases. These soils should have a high potential for removing phosphorus from solution since the double acid extractable phosphorus (Table 14) is much lower than the calculated or estimated phosphorus adsorption maximum.

#### B. Effect of Aerobic and Anaerobic Conditions on Phosphorus Adsorption

This experiment was conducted on a similar manner to the preceeding one with the same soil samples, except the soils used in this study were preincubated under either aerobic or anaerobic conditions. Samples in the previous study were not preincubated; therefore, this study was conducted to determine the effect of preincubation as well as aeration effects. In the aerobic preincubation soils were treated with deionized water to obtain about field capacity, while soils were saturated with deionized water for the anaerobic preincubation. Phosphorus sorption isotherms (Figures 22-27) constructed for the six soils from the two experimental sites indicate that the amount of phosphorus sorbed by the soil complex varied with soil type and the sorption behavior in certain soils was influenced by aerobic and anaerobic soil conditions. The adsorption isotherms for the aerobic treatment and isotherms obtained from the previous adsorption study were approximately the same as expected except for the Myakka adsorption isotherm. The differences in the Myakka adsorption isotherm will be discussed later. In the Basinger soil (Figure 22) less phosphorus was adsorbed under anaerobic than aerobic treatments over almost the entire range of solution phosphorus concentrations. However, at the lower concentrations, the difference was smaller than at high solution phosphorus concentrations. With

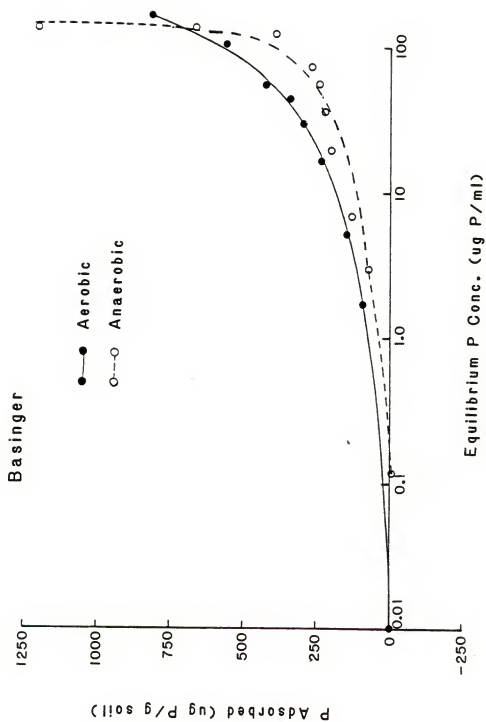


Figure 22. Adsorption of P by Basinger soil under aerobic and anaerobic conditions.

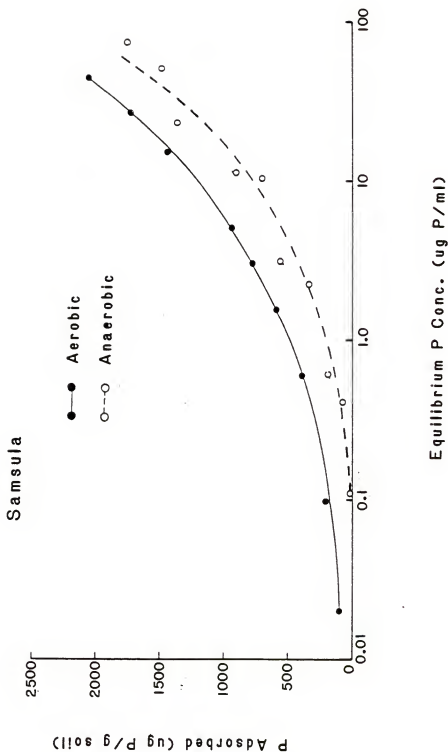


Figure 23. Adsorption of P by the Samśula soil under aerobic and anaerobic conditions.

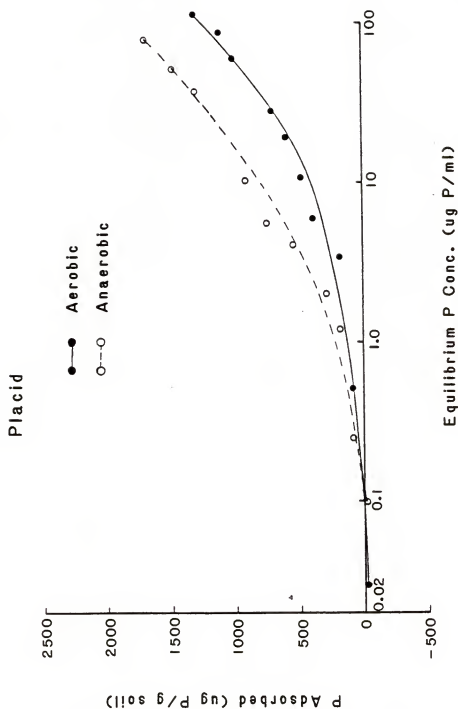


Figure 24. Adsorption of P by the Placid soil under aerobic and anaerobic conditions

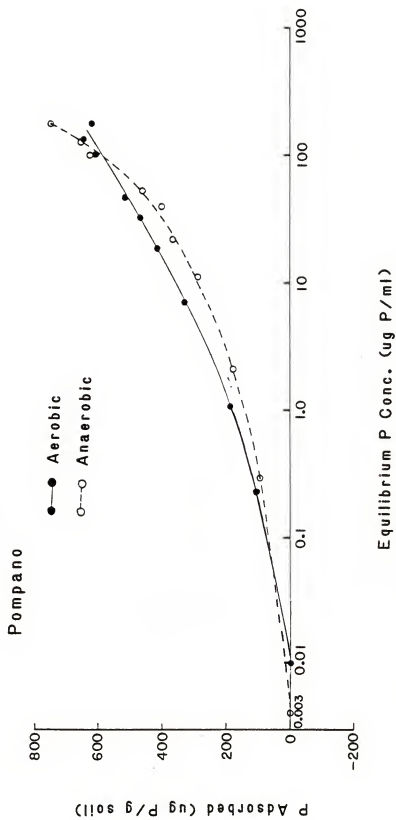


Figure 25. Adsorption of P by the Pompano soil under aerobic and anaerobic conditions.

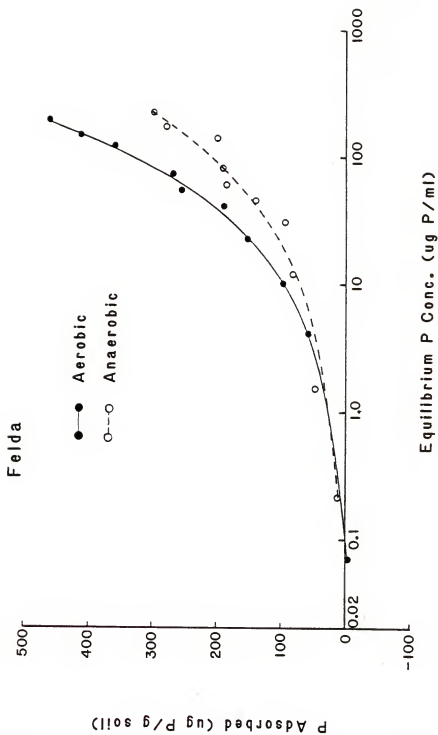


Figure 26. Adsorption of P by the Felda soil under aerobic and anaerobic conditions.



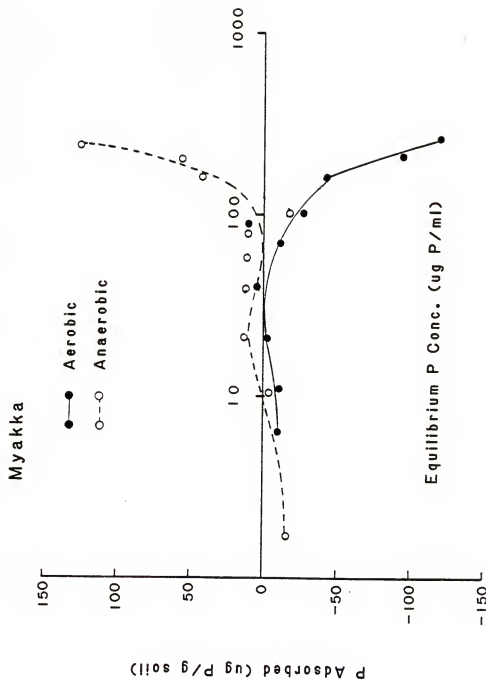


Figure 27. Adsorption of P by the Myakka soil under aerobic and anaerobic conditions.

a solution phosphorus concentration of  $0.5 \mu\text{g P/ml}$ , which is in a range commonly found in the overlying water of wetland areas, adsorbed phosphorus was about 52 and  $20 \mu\text{g P/g soil}$  under aerobic and anaerobic conditions, respectively. The equilibrium phosphate concentration (EPC), that condition at which phosphorus is neither gained or lost by soil, was also affected by aerobic and anaerobic conditions. From the sorption isotherms, the EPC was found to be in the range of 0.01 to 0.02 and 0.18 to  $0.23 \mu\text{g P/ml}$  for aerobic and anaerobic conditions, respectively. At a solution phosphorus concentration of about  $100 \mu\text{g P/ml}$ , the adsorption curve for anaerobic conditions showed a sharp increase in the amount of phosphorus being adsorbed. This sharp increase in apparent phosphorus sorption was not likely due to an adsorption reaction but was more likely due to a precipitation reaction forming a solid phase such as ferrous phosphate compound.

The effect of aerobic and anaerobic conditions on phosphorus adsorption characteristics of the Samsula soil was similar to the Basinger soil, i.e., less phosphorus was adsorbed under anaerobic conditions (Figure 23). However, there was not the apparent precipitation phenomenon observed at the high phosphorus concentration and there was a greater and more consistent difference between aerobic and anaerobic conditions with the Samsula soil. At a solution phosphorus concentration of  $0.5 \mu\text{g P/ml}$ , about 350 and  $150 \mu\text{g P/g soil}$  were sorbed under aerobic and anaerobic conditions, respectively.

In contrast to the Basinger and Samsula soils, the Placid soil sorbed more phosphorus under anaerobic than aerobic conditions when solution phosphorus concentration was higher than about  $0.2 \mu\text{g P/ml}$

(Figure 24). Below  $0.2 \mu\text{g P/ml}$  the difference between the two systems was insignificant. With  $0.5 \mu\text{g P/ml}$ , 90 and  $120 \mu\text{g P/g}$  soil was adsorbed under aerobic and anaerobic conditions, respectively. Small amounts of native phosphorus was desorbed when solution phosphorus concentration was low. The EPC of Placid soil ranged from 0.04 to 0.07 and 0.1 to  $0.2 \mu\text{g P/ml}$  under aerobic and anaerobic conditions, respectively.

Phosphorus sorption characteristics of the Pompano soil (Figure 25) was similar to the Basinger soil. At low solution phosphorus concentrations, the difference in phosphorus sorbed under aerobic or anaerobic conditions was negligible. However, at high solution phosphorus ( $100 \mu\text{g P/ml}$ ) there was more phosphorus sorbed under anaerobic than aerobic conditions with some indications of precipitation occurring above  $100 \mu\text{g P/ml}$ . The amount of phosphorus sorbed by the Pompano soil when the solution phosphorus concentration was  $0.5 \mu\text{g P/ml}$ , was 138 and  $105 \mu\text{g P/g}$  soil for aerobic and anaerobic conditions, respectively.

In the Felda soil, lower phosphorus was adsorbed under anaerobic than aerobic conditions (Figure 26). Phosphorus sorption anaerobic and aerobic conditions increased with increasing phosphorus concentration. Compared to the previous soils, much lower phosphorus was adsorbed (about  $10 \mu\text{g P/g}$  soil under both conditions), at a solution phosphorus concentration of  $0.5 \mu\text{g P/ml}$ . The EPC of Felda soil was approximately  $0.1 \mu\text{g P/ml}$  under both conditions.

Due to the low phosphorus adsorptive capacity of Myakka soil as shown in Table 14, the adsorption isotherms for this soil were different from the isotherms for the other soils investigated (Figures 27). At solution phosphorus levels lower than  $100 \mu\text{g P/ml}$ , the amount of phosphorus adsorbed was quite low and assumed to be negligible under

both aerobic and anaerobic conditions. Some phosphorus was found to be sorbed under anaerobic conditions when solution phosphorus was higher than 100  $\mu\text{g P/ml}$ ; however, the amount sorbed was much smaller than that sorbed by the other soils. A considerable amount of phosphorus was released from the soil under aerobic conditions when solution phosphorus concentration was higher than 100  $\mu\text{g P/ml}$ . In this soil, the adsorption isotherm under aerobic treatment was also different from the isotherm obtained from the air dried soil in the previous study. This unexpected difference might have been caused by the pretreatment. There is no obvious mechanism to explain this type of reaction. In contrast, under anaerobic conditions, there was definite indication of phosphorus precipitation.

Even though there were differences in phosphorus sorption under aerobic and anaerobic conditions, the capacity of soils to sorb phosphorus under these conditions was very high, except for Myakka soil, as compared to the amount of native phosphorus present (Table 14). Therefore, this study indicates that these wetland soils under either aerobic or anaerobic conditions should remove large amounts of phosphorus from agricultural drainage water.

Based on the phosphorus adsorption data (Table 14), the characteristics of soils (Table 14), and cation levels in equilibrium solutions (Table 15), the mechanism of phosphorus sorption seemed to be varied among the investigated soils. For all soils except Placid and Myakka soils, an Al-organic matter  $-\text{PO}_4^{-3}$  complex was probably responsible for the phosphorus sorption as indicated by relatively high aluminum and organic matter in these soils and relatively high phosphorus adsorption under both aerobic and anaerobic conditions. Iron might have some role in

TABLE 15

VALUES OF CATION CONCENTRATION AND pH OF THE EQUILIBRIUM  
SOLUTIONS AFTER 24 HOURS OF EQUILIBRATION UNDER  
AEROBIC AND ANAEROBIC CONDITIONS

Soil	Aerobic				Anaerobic			
	Al	Fe	Mn	pH	Al	Fe	Mn	pH
	- - - - ppm - - -				- - - - ppm - - -			
Samsula	3.2	0.36	0.12	4.0	3.9	27.74	0.110	4.7
Placid	0	0.04	0.003	5.7	1.0	7.56	0.021	6.4
Basinger	1.7	0.25	0.01	3.2	2.0	15.23	0.031	4.2
Pompano	1.9	0.18	0.01	3.4	1.2	59.85	0.020	4.3
Felda	0	0.10	0.02	4.2	0.50	7.60	0.015	5.0
Myakka	1.0	0.10	0.006	3.2	1.0	3.06	0.029	3.9

phosphorus retention, i.e. precipitation of ferrous phosphate or phosphorus sorption involving ferrous hydroxide ( $\text{Fe}(\text{OH})_2$ ), in the Basinger and Pompano soils as evidenced by high double acid extractable iron (Table 14), high levels of soluble iron in anaerobic equilibrium solutions (Table 15), and the increase in phosphorus adsorption under anaerobic conditions at very high solution phosphorus concentrations. Similar results were found in a Sharkey soil investigated by Khalid et al. (1977). They attributed the greater phosphorus sorption under reduced conditions to an increase in sorption sites due to the transformation of ferric hydroxide ( $\text{Fe}(\text{OH})_3$ ) to ferrous hydroxide ( $\text{Fe}(\text{OH})_2$ ) under reduced condition. Unlike iron, aluminum does not easily change its species under different redox conditions. An Al-organic matter- $\text{PO}_4^{-3}$  complex seemed to play a major role in Samsula, Basinger, Pompano, and Felda soils as indicated by the small difference between phosphorus adsorption under aerobic and anaerobic conditions.

The Placid soil seemed to have a different phosphorus adsorption mechanism. A reversed pattern of phosphorus sorption was observed, i.e., higher phosphorus sorption under anaerobic conditions for almost all concentrations of solution phosphorus. The Placid soil also contained relatively low aluminum and iron levels, but was high in calcium content. Therefore, phosphorus sorption in this soil may be attributed to  $\text{Ca-PO}_4^{-3}$  interaction as evidenced by the increase of phosphorus sorption at the higher pH of the anaerobic treatment (Moreno et al., 1960; Stumm and Morgan, 1970; Reddy and Graetz, 1981).

### C. Phosphorus Removal from Overlying Water in Soil-Water Columns

Soil-water columns were used as a simulated wetland system to study phosphorus removal from the overlying water by wetland soils. Soils used in this study were collected from the Armstrong site and their characteristics are presented in Table 1. It should be noted that some characteristics of the soils used in this study differed slightly from the soils used in the preceeding phosphorus studies because they were collected at a different time and also at slightly different locations.

Values for orthophosphate, dissolved oxygen, and pH in the overlying water of the phosphorus amended and control soil-water columns are presented in Table 16. Dissolved oxygen levels stayed near saturation at all times due to artificial aeration. The pH remained relatively stable in the Basinger and Samsula soils and generally decreased in the other soils. Orthophosphate removal from overlying water of the soil water columns during an incubation period of 25 days is also presented graphically in Figure 28. The fastest phosphorus removal rate was observed in the Placid soil-water column with a removal rate of 0.08  $\mu\text{g P/ml/day}$ , while the Basinger and Samsula soil-water columns showed slower phosphorus removal rates of 0.05  $\mu\text{g P/ml/day}$  each. After 25 days, 88, 61, and 54% of the initial phosphate was removed from the overlying water in the Placid, Basinger, and Samsula soil-water, respectively. Even though Samsula soil was found to have highest adsorption maximum in the previous study, the low phosphorus removal rate observed in this soil system is probably due to fewer adsorption sites on a volume basis as a result of lower bulk density of the

TABLE 16

ORTHOPHOSPHATE, DISSOLVED OXYGEN, AND pH VALUES MEASURED IN THE  
OVERLYING WATER OF SOIL-WATER COLUMNS WITH AND WITHOUT  
ADDITION OF 1,000  $\mu\text{g P}$  AS POTASSIUM PHOSPHATE,  
INCUBATED FOR 25 DAYS

Treatment	Days					
	0	2	5	10	15	25
----- $\text{PO}_4^{3-}\text{-P}$ , $\mu\text{g P/ml}$ -----						
Control Basinger	0.29	0.21	0.16	0.03	0.02	<0.01
Control Placid	0.17	0.06	<0.01	<0.01	<0.01	<0.01
Control Samsula	0.50	0.47	0.41	0.39	0.25	0.10
Treated Basinger	2.19	1.77	1.60	1.20	1.07	0.85
Treated Placid	2.29	1.63	1.30	0.88	0.65	0.27
Treated Samsula	2.46	2.16	2.00	1.77	1.72	1.12
----- Dissolved oxygen, ppm -----						
Control Basinger	7.2	7.6	7.4	7.7	7.2	7.4
Control Placid	7.3	7.6	7.2	7.6	7.4	7.4
Control Samsula	7.2	7.5	7.2	7.7	7.3	7.1
Treated Basinger	7.4	7.7	7.5	7.4	7.3	7.4
Treated Placid	7.0	7.7	7.5	7.4	7.4	7.3
Treated Samsula	7.3	7.7	7.4	7.5	7.3	7.4
----- pH -----						
Control Basinger	5.6	5.4	5.5	6.1	6.2	5.4
Control Placid	5.2	4.8	4.5	5.3	4.4	4.2
Control Samsula	6.9	6.8	6.7	7.0	7.1	7.0
Treated Basinger	5.3	5.0	4.8	5.3	5.1	4.9
Treated Placid	5.6	5.4	4.8	5.3	4.9	4.6
Treated Samsula	6.6	6.7	5.7	5.7	5.3	5.3



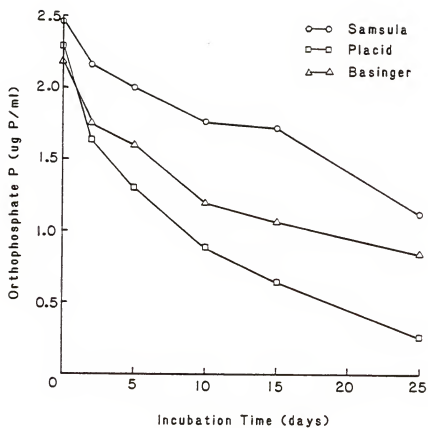


Figure 28. Orthophosphate disappearance in the overlying water of three soil-water columns.

Samsula soil in the column. These results indicate that phosphorus can be removed by wetland soils very efficiently.

These were the same columns used in the nitrification study. Recall that the soil columns were sectioned and extracted with KCl to remove various nitrogen species. Phosphorus extracted by KCl was also measured. The distribution of KCl extractable phosphorus in the underlying soil after 25 days is re shown in Figure 29. Only trace amounts of KCl extractable phosphorus was found in the control soil columns (data not presented). In the Basinger and Samsula soil columns amended with phosphorus, it was found that most of the phosphorus was sorbed in the top 2 cm of the soil. Soil phosphorus concentrations ranged from 0.23 to 5.02  $\mu\text{g P/g soil}$ . Below 2 cm phosphorus concentrations were generally  $<0.1 \mu\text{g P/g soil}$ . Only a small amount of KCl extractable phosphorus was found in the Placid soil column, which is in contradiction to the previous results of the Placid soil having the highest rate of phosphorus removal from the overlying water. These contradictory results might be due to the use of KCl as the extracting solution. If phosphorus is retained by the Placid soil via  $\text{Ca-PO}_4^{-3}$  interaction as discussed earlier, KCl likely cannot extract phosphorus from the  $\text{Ca-PO}_4^{-3}$  complex in the soil, since this extractant is generally used for more soluble nutrients.

With the low recovery of added phosphorus as found by using the KCl extractant, the soil sections were dried and re-extracted with double acid extractant. Much higher quantities of phosphorus were extracted as shown in Figure 30. The treated Samsula and Placid soils showed a definite increase in extractable phosphorus to a depth of 1 to 1.5 cm. The control and treated Basinger soils did not have a differing level

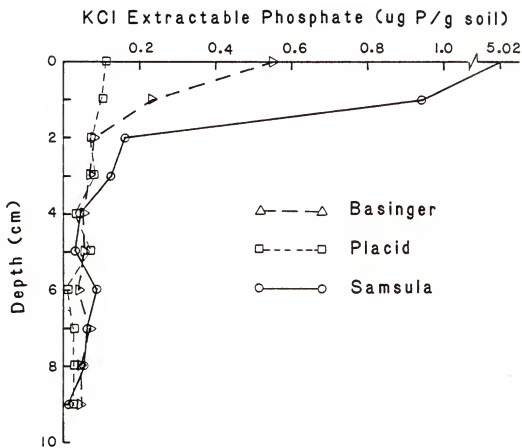


Figure 29. Distribution of KCl extractable P in the soil columns with added P.

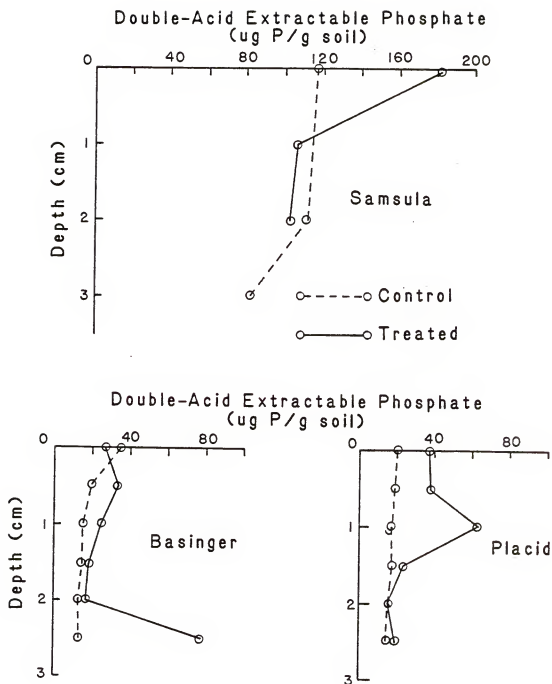


Figure 30. Distribution of double-acid extractable phosphate in the soil columns.

of extractable phosphorus at the surface but adsorption in the treated soil increased slightly to a depth of 2 cm where there was a major increase in adsorbed phosphorus. The reason for this increase cannot be ascertained from the data available but might be related to the interface between the aerobic and anaerobic zones in this soil.

### III. Nutrient Availability from Decaying Vegetation in Wetland Ecosystems

This investigation was conducted to evaluate the extent of nutrient release which might be expected when plants decay in wetland ecosystems. In these systems, where water levels are often low (<1m) and flow is slow, the characteristics of the underlying soil may have significant effects on the decomposition and associated nutrient regeneration from aquatic plant material. In this study, plant decomposition was measured in simulated wetland systems using 1) three soils of differing pH and organic matter content, and 2) reservoir water in the absence of soil.

#### A. Decomposition of Plant Material

Elemental composition (water extractable and total) of the plant material is shown in Table 17. Water extractable elements were determined as an indication of the extent of nutrient release due to solubilization which might be expected shortly after the decay process begins. With the exception of nitrate, potassium, and soluble organic carbon, all species measured were in the range of 100 to 600 µg/g of plant material. Nitrate levels were low, as expected, since most inorganic nitrogen in plant material is present as ammonium. Potassium is

TABLE 17

SELECTED CHARACTERISTICS OF PLANT MATERIAL USED IN THE STUDY

Parameter	Water Extractable	Total
	-----µg/g-----	%
Nitrate N	9	-
Ammonium N	137	-
Total Kjeldahl N	-	0.93
Orthophosphate P	105	-
Total P	-	0.10
Calcium	440	-
Magnesium	225	-
Potassium	2,800	-
Carbon	13,616	53
C:N	-	57.1

present in cell constituents in an unbound form and thus would be expected to be readily soluble which accounts for the 2,800  $\mu\text{g K/g}$  plant material. Soluble organic carbon was found to be 13,616  $\mu\text{g C/g}$  plant material, which is about 1.4% of plant material (by weight) or 2.6% of total carbon in plant material. This small amount of soluble organic carbon indicates that the major portion of plant material consists of insoluble organic carbon. The total carbon, nitrogen, and phosphorus contents of the plant material were 53, 0.93, and 0.10%, respectively. This gives a C:N:P ratio of 57:0.9:0.1. The high C:N ratio, 57:0.9, can effect the rate of decomposition and also the amount of nitrogen released. With a high C:N ratio, additional sources of nitrogen would be needed by the decomposer organisms in order to decompose the plant material. If sufficient additional nitrogen is not available, the nitrogen released from decaying plant material would then be assimilated by the decomposer organisms and the amount of nitrogen released to the overlying water would be decreased.

Organic carbon loss after decomposition for 16 weeks ranged from 18 to 53% under aerobic conditions (Figure 31). Losses under anaerobic conditions were not greatly different with a range of 20 to 47%. Data in figure 32 show dry weight loss of plant material after 16 weeks decomposition. Dry weight losses ranged from 15 to 47% and 18 to 45% under aerobic and anaerobic conditions, respectively. Organic carbon and dry weight losses followed similar trends (higher organic carbon loss with higher dry weight loss) in all systems except for the Basinger soil system. In this system, the organic carbon loss was higher in the anaerobic than in the aerobic systems, and the opposite was obtained for dry weight loss. These contradictory results may have been due to

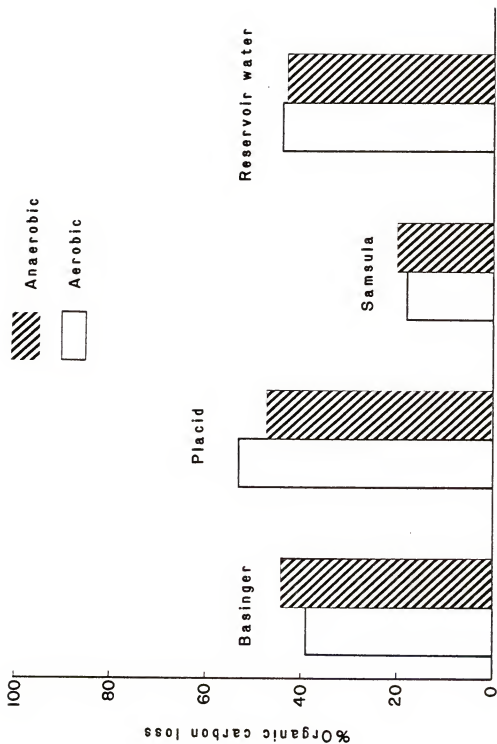


Figure 31. Loss of organic carbon from plant material after 16 week decomposition.



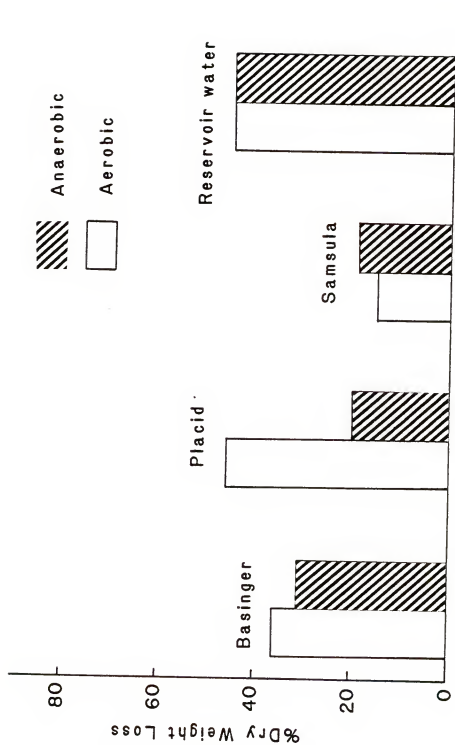


Figure 32. Dry weight loss of plant material after 16 week decomposition.

sediment which was not completely washed from the plant materials. However, aeration did not have a significant effect on plant decomposition rate as the rates were similar under aerobic and anaerobic conditions. This is in contrast to soils where decomposition is generally greater under aerobic conditions. Possibly the amount of oxygen present in aerated water (6-7 ppm) was sufficiently less than in aerated soil (21%) to account for the decomposition rate differences between soil and aquatic systems. Also, in these simulated aquatic systems, the plant material was in direct contact with the bottom sediments which may have been highly anaerobic particularly during the early phases of plant decomposition. However, a 50% loss in organic carbon in 16 weeks is still a significant decomposition rate for these aquatic systems. Since the effect of aeration varied among these systems, the decomposition rate of plant material was likely more dependent on factors other than the oxygen status of the systems.

Soil characteristics appeared to have a significant effect on the rate of plant decomposition. Organic carbon loss was in the order: Placid > Basinger > Samsula. This trend was obtained under both aerobic and anaerobic conditions. The pH of the overlying water, which in these systems was controlled to a large degree by the soil, appeared to affect the extent of organic residue decomposition. For example, the water pH of the aerobic system during the incubation period averaged 6.6, 4.9, and 4.2 for the Placid, Basinger, and Samsula soils, respectively (Table 18), which was also the order of decomposition rate. Only 18% of the organic carbon was lost in the Samsula soil system with a pH of 4.2 compared to 53% in the Placid soil system with a pH of 6.6. Decomposition in marsh water in the absence of soil, was

TABLE 18  
AVERAGE WATER pH DURING THE DECOMPOSITION PERIOD

Soil	Decomposition Conditions	
	Aerobic	Anaerobic
	- - - - - pH - - - - -	
Basinger	4.9	5.5
Placid	6.6	6.8
Samsula	4.2	4.4
Reservoir water	6.7	6.7

relatively rapid, also due to a favorable pH. This is in agreement with most previously reported research which has shown that decomposition of organic matter is most rapid in neutral or alkaline pH systems where bacteria are most active (Alexander, 1977). Bacteria growth is controlled in part by pH and since most of decomposition was likely due to bacteria, pH would have a controlling effect on decomposition rate.

Changes in nitrogen content of the decomposed material show that considerably less nitrogen than organic carbon was lost during decomposition. In fact, in two cases, nitrogen content increased during the decomposition process (Figure 33). There were no obvious trends in nitrogen loss or gain between aerobic and anaerobic systems. These data suggest that nitrogen was limiting in these systems and that additional nitrogen was likely obtained from the soil. In contrast to nitrogen, losses of phosphorus were greater than losses of organic carbon (Figure 34). Losses of phosphorus ranged from 42 to 62% under aerobic conditions and 37 to 64% under anaerobic conditions. The relatively greater amount of phosphorus loss was likely due to the fact that the plant material contained more than enough phosphorus to satisfy the needs of the decomposer population.

The loss of organic carbon with the reservoir water alone was 44 and 43% under aerobic and anaerobic conditions, respectively. This relatively high loss of organic carbon can be partly attributed to the higher pH (i.e., 6.7 in both aerobic and anaerobic conditions). Larger amounts of nitrogen and phosphorus were lost under anaerobic conditions in the reservoir water. The losses of nitrogen and phosphorus were 32 and 72%, respectively, under anaerobic conditions and 11 and 52% under aerobic conditions.

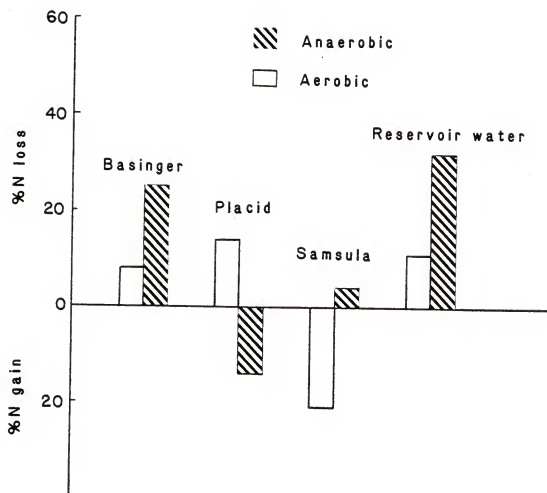


Figure 33. Loss or gain of nitrogen from plant material after 16 week decomposition.

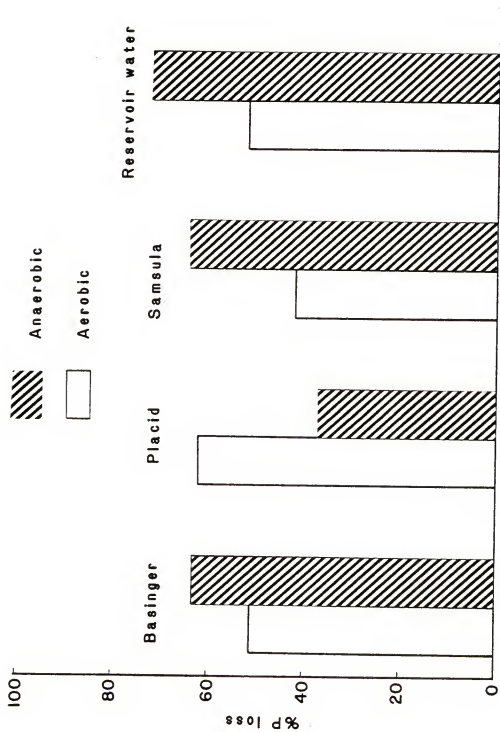


Figure 34. Loss of phosphorus from plant material after 16 week decomposition.

The release of nutrients such as nitrogen and phosphorus during the decomposition process will be affected by the concentration of these elements in the plant as well as the bacterial nutrient requirements. In these studies, decomposition was limited by nitrogen and thus only relatively small amounts of nitrogen were lost from the decaying organic material. Because of the high C:N ratio of the plant material, the nitrogen level in the decomposing plants were too low to support the decomposer population; therefore, as nitrogen was released from plant material it was recycled to organic nitrogen by the microbial population. This would result in nitrogen accumulation in decomposing plant tissues during the decomposition process as was also observed by several workers (Davis and Van der Valk, 1978; Nichols and Keeney, 1973; Puriveth, 1980; Hunter, 1976). In contrast, where phosphorus was not limiting, significant amounts (generally about half of the total phosphorus) were released from the decaying plant material.

#### B. Release of Nutrients to Overlying Water

Conductivity of the overlying water is shown in Table 19. Conductivity is an indication of the amount of salts present in the water which is a reflection of nutrient release from the plant material and/or soil. The conductivity of the reservoir water in the absence of soil increased approximately 5 fold during the first week of incubation and then remained relatively constant during the remainder of the incubation period. This indicates that a major portion of the nutrients released from decaying plant material appears to be released shortly after decomposition starts. This rapid release of soluble nutrients from the plant material is likely due to physical release or solubilization rather

TABLE 19

INFLUENCE OF SOIL TYPE AND AERATION ON CONDUCTIVITY AND pH IN OVERLYING WATER OF SYSTEMS WITH AND WITHOUT PLANT MATERIAL

Incubation Time	Basinger		Placid		Samsula		Reservoir Water						
	Aerobic A <sup>a</sup>	Anaerobic B <sup>b</sup>	Aerobic A	Anaerobic B	Aerobic A	Anaerobic B	Aerobic A	Anaerobic B					
weeks	Conductivity (micro mhos per cm)												
0	69	61	60	58	62	67	59	63	54	56	55	82	83
1	63	213	61	265	69	353	60	365	61	175	59	415	435
2	71	225	63	275	71	280	64	390	88	150	65	325	375
4	85	203	71	295	71	258	74	385	100	150	80	360	390
6	99	193	75	303	62	240	73	300	80	145	73	330	370
8	110	210	79	290	76	275	85	275	83	150	70	380	410
12	110	210	95	290	84	230	71	245	77	150	72	420	440
16	111	240	120	310	93	235	82	225	78	160	77	415	440
pH													
0	4.1	4.1	4.1	4.3	7.3	7.3	7.2	7.4	4.1	4.1	4.1	6.8	7.0
1	4.1	5.2	4.1	5.1	5.7	6.2	6.0	6.4	4.5	4.4	4.2	5.0	4.9
2	4.5	5.5	4.3	5.7	5.3	5.9	5.5	6.1	3.7	4.7	4.0	6.1	6.1
4	4.6	5.5	4.3	6.3	6.2	5.8	5.3	6.6	3.7	4.5	3.9	6.3	5.8
6	4.5	5.1	4.8	5.7	5.4	5.4	5.4	5.6	3.8	4.2	4.2	5.3	5.7
8	4.1	4.7	4.4	6.1	7.3	7.6	7.5	7.8	4.0	4.0	4.1	7.9	7.9
12	4.1	4.6	4.5	5.5	7.3	7.5	6.7	7.6	3.8	3.9	4.3	8.1	8.3
16	4.0	4.7	4.5	5.3	7.2	7.2	7.2	7.0	3.9	4.0	3.9	8.0	8.1

<sup>a</sup> A and B represent systems without and with added plant material, respectively.



than microbial processes. Ions such as potassium, magnesium, and calcium are often present in soluble form in plant cell contents and are readily released upon plant death. Hill (1979) and Puriveth (1980) also observed drastic decreases in dry weight and nutrient levels in decomposing macrophytes during the first phase, 0-30 days, of decomposition due to rapid leaching of soluble nutrients. The conductivity of the anaerobic systems was slightly higher than the aerated system suggesting slightly greater nutrient release.

In the soil-water systems, the conductivity is due to ions both from the soil and the plant material. Conductivity from the three soil systems without plant material showed approximately the same trends, i.e., initial values averaged 60  $\mu\text{mho/cm}$  and after 16 weeks the average increased to 94 for the aerobic systems and 93 for the anaerobic systems. The conductivity of the soil-water systems containing plant material reflected the organic carbon loss pattern shown in Figure 31, i.e., conductivity was lowest in the Samsula system and highest in the Placid system.

The pH of overlying water in the soil-water systems generally reflected the soil pH values with the Placid system having the highest pH followed by the Samsula and Basinger systems (Table 19). The reservoir water system had an initial pH around neutrality but decreased with time likely due to the solubilization of organic acids as indicated by the increase in soluble organic carbon concentration in the overlying water one week after material addition (Table 20). After the organic acids were broken down by the microbial population, the pH again increased to about 8 during the latter part of the incubation period. A similar trend was observed in the Placid system. However, the Samsula

TABLE 20

INFLUENCE OF SOIL TYPE AND AERATION ON SOLUBLE ORGANIC CARBON CONCENTRATION IN OVERLYING WATER OF SYSTEMS WITH AND WITHOUT PLANT MATERIAL

Incubation Time Weeks	Baninger				Flacid				Samuela				Reservoir Water			
	Aerobic		Anaerobic		Aerobic		Anaerobic		Aerobic		Anaerobic		Aerobic		Anaerobic	
	A <sup>a</sup>	B <sup>a</sup>	A	B	A	B	A	B	A	B	A	B	A	B	A	B
	- 100 µg OC-C per ml -															
0	85.7	74.7	79.5	108.0	63.8	88.8	108.0	55.0	81.6	100.6	77.9	125.7	-	83.0	-	46.5
1	122.2	189.3	124.5	200.7	99.7	169.0	111.1	147.0	101.6	128.0	121.6	164.4	-	202.2	-	238.7
2	135.7	179.3	133.8	177.0	55.8	144.4	88.8	150.0	82.6	127.1	79.3	122.3	-	137.4	-	132.0
4	151.3	211.8	125.0	239.2	104.5	128.1	93.7	124.0	85.5	151.1	118.8	151.6	-	132.8	-	232.7
6	251.6	310.9	287.2	380.1	173.0	139.9	113.7	156.3	98.4	136.8	156.5	159.0	-	158.9	-	250.0
8	213.5	256.6	223.5	373.4	161.0	180.1	152.2	181.3	118.6	122.0	162.6	182.0	-	177.7	-	223.1
12	300.4	341.6	316.8	541.9	168.0	209.3	179.9	190.3	153.9	172.9	165.0	206.2	-	266.7	-	252.7
16	90.5	252.3	230.6	406.2	119.1	135.9	118.3	174.2	163.9	102.5	158.1	174.0	-	162.1	-	211.5
Avg.	168.8	227.1	189.7	315.0	116.0	149.1	121.2	147.4	133.1	129.8	130.4	160.0	-	165.2	-	198.3

<sup>a</sup>A and B represent systems without and with added plant material, respectively.

and Basinger systems which started out with a low initial pH tended to increase in pH possibly because the organic acids released had a higher  $pK_a$  than the initial soil system.

In the systems with plant material, soluble organic carbon concentrations in the overlying water increased from 2 to 5 fold during the first week of incubation. This increase was probably due to the release of readily soluble carbon from the added plant material as well as from the soil. The highest increase of soluble organic carbon was in the system with reservoir water only. In the systems containing soil without added plant material, similar amounts of soluble organic carbon were released for the three soil types. Average concentration over the 25 day incubation period ranged from 113 to 196  $\mu\text{g C/ml}$  under aerobic conditions and 130 to 227  $\mu\text{g C/ml}$  under anaerobic conditions. As expected, addition of plant material increased the concentration of soluble organic carbon in the overlying water. Increases of 15 to 34% were observed under aerobic conditions with slightly larger increases (21 to 65%) found under anaerobic conditions. The Basinger soil system always had the highest soluble carbon levels suggesting that there was greater release of carbon from the soil itself and also less interaction between soluble carbon release from the added plant material and the soil.

Ammonium and TKN values are shown in Table 21. In the reservoir water, the highest ammonium concentrations in the absence of soil were measured after the first week of incubation with the anaerobic system having the highest concentration. The ammonium concentration in the reservoir water declined to generally less than 1  $\mu\text{g N/ml}$  during the rest of the incubation period for both aerobic and anaerobic systems.

TABLE 21

INFLUENCE OF SOIL TYPE AND AERATION ON AMMONIUM AND TOTAL KJELDAHL NITROGEN CONCENTRATIONS IN OVERLYING WATER OF SYSTEMS WITH AND WITHOUT PLANT MATERIAL

Incubation Time weeks	Bas Inger		Placid		Samula		Reservoir Water	
	Aerobic A	Anaerobic B	Aerobic A	Anaerobic B	Aerobic A	Anaerobic B	Aerobic A	Anaerobic B
- - - - - $\mu\text{g NH}_4\text{-N per ml}$ - - - - -								
0	1.05	1.66	1.53	1.99	0.10	0.14	0.35	0.20
1	2.30	2.08	1.70	7.55	0.34	1.88	0.43	0.20
2	6.46	11.58	7.60	13.18	0.50	0.68	0.90	3.18
4	2.71	2.35	3.35	19.75	0.13	4.03	0.85	1.23
6	2.01	2.72	4.23	24.25	0.08	0.06	1.24	6.03
8	0.10	0.35	4.55	1.98	0.08	0.05	1.70	4.46
12	0.25	0.24	0.60	2.80	0.30	0.21	0.65	2.00
16	1.23	2.67	0.47	0.16	0.21	0.37	0.87	1.62
- - - - - $\mu\text{g TN per ml}$ - - - - -								
0	5.08	5.17	5.43	5.26	3.25	3.34	4.16	2.98
2	10.17	12.27	10.08	25.95	4.12	4.56	3.86	7.72
4	6.66	10.43	8.15	28.49	4.47	8.06	5.00	6.14
8	3.86	10.08	11.22	29.27	4.82	5.26	15.25	12.88
16	3.33	11.66	16.57	34.53	4.73	5.61	8.77	7.10
- - - - - $\mu\text{g NH}_4\text{-N per ml}$ - - - - -								
0	1.73	1.69	1.77	1.75	1.73	1.69	1.77	1.75
1	1.33	2.63	1.88	3.35	1.33	2.63	1.88	3.35
2	0.58	3.91	2.33	2.55	0.58	3.91	2.33	2.55
4	0.11	2.40	1.53	2.88	0.11	2.40	1.53	2.88
6	0.28	1.53	1.65	3.60	0.28	1.53	1.65	3.60
8	0.08	0.26	1.60	4.43	0.08	0.26	1.60	4.43
12	0.33	0.35	1.73	4.88	0.33	0.35	1.73	4.88
16	0.20	0.13	0.45	5.70	0.20	0.13	0.45	5.70
- - - - - $\mu\text{g TN per ml}$ - - - - -								
0	4.25	4.38	4.38	4.38	4.25	4.38	4.38	4.38
2	4.60	10.80	4.60	10.80	4.60	10.80	4.60	10.80
4	1.55	7.54	1.55	7.54	1.55	7.54	1.55	7.54
8	0.29	3.95	0.29	3.95	0.29	3.95	0.29	3.95
12	0.18	5.26	0.18	5.26	0.18	5.26	0.18	5.26
16	0.25	6.93	0.25	6.93	0.25	6.93	0.25	6.93

° A and B represent systems without and with added plant material, respectively.

This loss of ammonium was likely due to uptake of nitrogen by the microbial population responsible for the decay process. The microbial assimilation of nitrogen is also suggested by the decrease in soluble organic carbon after the first week of incubation mentioned earlier. Some ammonium loss may also be due to denitrification as indicated by the low nitrate concentration in the aerobic system (generally  $1 \mu\text{g N/ml}$ ). However, this would not explain the decreases in the anaerobic system. Ammonia volatilization may also explain part of the decrease although the water pH did not go above 7 until the 8th week. Total Kjeldahl nitrogen, which includes ammonium plus soluble organic nitrogen, also increased initially but then remained relatively steady during the incubation period.

In all soil-water systems with added plant material, ammonium concentrations were approximately three times higher than the systems without plant material added (Table 21). Highest ammonium concentrations were observed in the Basinger soil-water system either with or without plant addition. There was evidence that ammonium in the overlying water in the Basinger system was apparently released from the underlying soil. Ammonium concentrations were higher under anaerobic than aerobic conditions in all soil-water systems. This may be due to lower uptake of ammonium by microorganisms under anaerobic conditions. Nitrification, and subsequent denitrification, may also have caused lower ammonium concentrations in the aerobic systems.

About half of the TKN in the overlying water in the systems with added plant material was released from the underlying soil (Table 21). Highest TKN concentration was found in the Basinger soil-water system with added plant material, especially under anaerobic conditions,

which was a result of the high loss of nitrogen from plant material in this system. Considerable lower amounts of TKN were observed in the Placid and Samsula overlying waters, probably due to the recycling of nitrogen into microbial biomass. Higher TKN in the overlying water was generally observed under anaerobic than aerobic conditions as a result of greater release of nitrogen from plant material and soil and slower nitrogen uptake by microorganisms under anaerobic conditions.

Orthophosphate and total phosphorus in the overlying water are shown in Table 22 and Figure 35. The orthophosphate concentration in the reservoir water without soil is indicative of the amount of phosphorus released from the decomposing plant material (Figure 34). Comparison of total phosphorus and orthophosphate concentrations suggests that most of the phosphorus was present as orthophosphate. After the initial 2 weeks of incubation the orthophosphate concentration decreased to 1 to 2  $\mu\text{g}$  P/ml. Part of this decrease may have been due to assimilation of orthophosphate by microbes; however, an increase in total phosphorus, which would include organic phosphorus, was not observed. In fact, both orthophosphate and total phosphorus decreased with time. One possible explanation is that the water sampling procedure did not adequately sample microbial biomass which had settled to the bottom of the incubation vessel.

The effect of soil characteristics on phosphorus release to the overlying water is readily apparent (Figure 35). The Samsula and Placid soils readily adsorbed most of the phosphorus released from the decaying plant material with only small amounts being released to the overlying water. The Basinger soil has a lower adsorptive capacity than the other two soils, as observed in the previous phosphorus adsorption experiments.

TABLE 22

INFLUENCE OF SOIL TYPE AND AERATION ON ORTHOPHOSPHATE AND TOTAL PHOSPHORUS CONCENTRATIONS IN OVERLYING WATER OF SYSTEMS WITH AND WITHOUT PLANT MATERIAL

Incubation Time weeks	Basinger		Placid		Samsula		Reservoir Water	
	Aerobic A <sup>b</sup>	Anaerobic B <sup>b</sup>	Aerobic A	Anaerobic B	Aerobic A	Anaerobic B	Aerobic A	Anaerobic B
mg PO <sub>4</sub> -P per ml								
0	0.1	0.1	0.1	0.1	0.10	0.10	-	-
1	0.1	0.7	0.1	0.9	0.25	0.15	T	T
2	5.4	9.7	9.4	10.0	0.35	0.40	0.27	-
4	0.5	1.3	0.1	2.3	0.10	0.10	5.35	8.35
6	0.5	1.6	1.0	1.6	0.10	0.10	1.40	3.15
8	0.8	1.4	1.2	2.2	0.10	0.10	0.70	2.25
12	0.6	1.0	1.4	3.8	0.20	0.25	1.15	1.85
16	1.3	2.0	2.4	2.3	0.40	0.35	1.90	2.00
					0.30	0.20	0.80	1.35
mg Total P per ml								
0	0.10	0.10	0.10	0.10	0.10	0.10	-	-
2	5.80	11.00	10.50	11.50	0.40	0.48	0.10	0.10
4	0.50	1.40	0.10	2.70	0.10	0.15	6.68	9.50
8	0.80	0.50	1.20	1.80	0.20	0.25	1.80	2.88
16	1.30	0.30	2.40	1.80	0.30	0.20	1.30	2.75
					0.25	0.01	2.90	2.75

<sup>b</sup> A and B represent systems without and with added plant material, respectively.

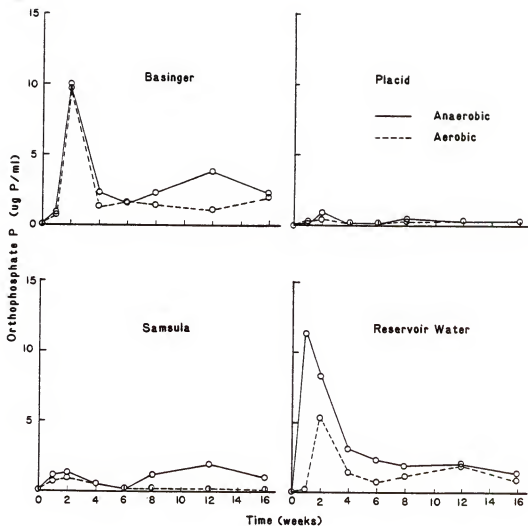


Figure 35. Concentration of orthophosphate in the water, with time from systems with plant material added.



The low adsorptive capacity resulted in higher concentrations of ortho-phosphate in the overlying water in the system containing plant material and also a greater release of phosphorus from soil without added plant material.

Calcium and potassium concentrations in the overlying water are shown in Table 23. Both elements were rapidly solubilized from the dead plant material as indicated by the higher concentrations in the reservoir water without soils. Little change occurred in concentration of either calcium or potassium during the 16 week incubation period in the absence of soil and concentrations were similar under aerobic and anaerobic conditions. In the soil-water systems, with the exception of the Placid soil, only small amounts of each element were released to the overlying water in the absence of added plant material. High concentrations of calcium (20  $\mu\text{g/ml}$ ) were released from the Placid soil due to the large amount of calcium present in that soil. Added plant material resulted in increased calcium and potassium concentrations in all soil-water systems with essentially no difference between aerobic and anaerobic systems.

A major portion of the nutrients released from decaying plant material appears to be released shortly after decomposition starts. In this study, highest nutrient concentrations in the overlying water were generally observed within 2 weeks after adding plant material. After this initial release of nutrients, the various interactions which take place between decaying plant material, microbes, and soil, affect the nutrient concentration in the overlying water. In most cases, there was a decrease in nutrients concentration in the overlying water with time as the nutrients were incorporated into the microbial biomass or were



adsorbed by the soil. This would suggest that nutrient losses from a wetland ecosystem such as a marsh would be affected by the residence time of water in the system. If initial decomposition occurred when the residence time was short, i.e., relative rapid water flow, more of the soluble plant nutrients would be flushed from the system. However, if the residence time was longer, there would be more of an opportunity for the nutrients to be reincorporated into the system.

In addition to affecting the plant decomposition rate, the soil also affected the extent of nutrient release to the overlying water, particularly for phosphorus. Phosphorus was readily adsorbed by two of the soils used in this study (Placid and Samsula) such that there was never a concentration over  $1 \mu\text{g P/ml}$  in the overlying water in contrast to over  $10 \mu\text{g P/ml}$  in the absence of soil. The double-acid extractable phosphorus values from soils used in this study before and after plant decomposition are compared in Table 24. Double-acid extractable phosphorus in the Placid and Samsula soil increased after plant decomposition, which indicates that a portion of the phosphorus released from decaying plant material was adsorbed by these soils. Double acid extractable phosphorus values for the Basinger soil indicate that a small quantity of phosphorus was lost from this soil. Nitrogen transformations are far more complex than those of phosphorus and the effect of soil characteristics on nitrogen concentrations in the overlying water was much more variable. Since nitrogen was the limiting nutrient for decomposition in these systems, most of the released nitrogen appeared to be recycled into the decaying plant material. There was some evidence that nitrification-denitrification might have been responsible for nitrogen loss in the aerobic Placid soil. Other nutrients

TABLE 24

COMPARISON OF DOUBLE-ACID EXTRACTABLE P, K, AND Ca FROM  
SOIL BEFORE AND AFTER DECOMPOSITION OF PLANT MATERIAL

System	Double-Acid Extractable		
	P	K	Ca
	----- $\mu\text{g/g soil}$ -----		
Initial			
Basinger	3.3	34	98
Placid	2.1	30	2,800
Samsula	1.6	17	520
Final			
Basinger			
Aerobic	3.2	80	260
Anaerobic	2.7	68	140
Placid			
Aerobic	2.1	112	3,000
Anaerobic	2.7	80	2,600
Samsula			
Aerobic	4.1	192	720
Anaerobic	5.4	204	760

such as calcium and potassium were apparently retained in small amounts by the soil cation exchange sites as indicated in Table 24, i.e., higher amounts of these nutrients were extracted from soils at the end of the decomposition period, but significant amounts were also present in the overlying water throughout the incubation period.

## CHAPTER V

### SUMMARY AND CONCLUSIONS

A series of laboratory experiments were conducted to evaluate the effectiveness of soil in wetland retention/detention areas for removing nutrients from agricultural drainage water around the Kissimmee River Basin.

Denitrification potentials of the soils were evaluated by determining the extent of denitrification in the soil in the absence of overlying water. In this experiment  $^{15}\text{N}$  labeled nitrate was added directly to the soil matrix. Over 90% of the nitrate was lost from the soil within a 2-to 6-day period. From the recovery of labeled nitrate, it was found that less than 3% of added nitrate was reduced to ammonium and less than 1.5% was immobilized into organic nitrogen. At least 96% was unaccounted for and presumably was lost via denitrification.

Further investigations on nitrification and denitrification were made in simulated wetland systems. In the nitrification study,  $^{15}\text{N}$  labeled ammonium was added to the overlying water of soil-water columns, whereas  $^{15}\text{N}$  labeled nitrate was added to the overlying water in the denitrification experiment. Nitrification was an important process involved in removal of ammonium from the agricultural drainage water as long as the pH of the system was above 5. Ammonium removal from the overlying water in the soil-water columns ranged from 43 to 84% after 25 days. A portion of the ammonium loss (5 to 12%) was due to

immobilization which was found to be highest in the systems with high amounts of available carbon. Ammonium (5%) was also adsorbed by underlying soil. About 50% of the added ammonium was not accounted for, likely due to nitrification and subsequent denitrification to nitrogen gas. Ammonium removal rates in these systems were estimated to range from 0.31 to 0.63  $\mu\text{g N/ml/day}$ .

Denitrification rates in the soil-water systems were slower than in the systems without overlying water. When nitrate is present in the overlying water, the denitrification rate is likely controlled by diffusion of nitrate from the overlying water into the underlying soil where nitrate is denitrified. After 25 days, considerable amounts of nitrate were removed from the overlying water. Amounts ranged from 45 to 62% of added nitrate, with higher nitrate removal rates in the systems with higher pH and organic matter contents. Generally, small amounts of labeled nitrate was recovered as ammonium and organic nitrogen. The unaccounted-for nitrate was likely lost from the soil-water systems due to denitrification. The calculated first-order denitrification rate constants ( $k$ ) based on labeled nitrate ranged from 0.02 to 0.062  $\text{day}^{-1}$ . These values are equivalent to the nitrate removal rates of 300 to 930  $\text{g/ha/day}$ , assuming a nitrate concentration of 10  $\mu\text{g N/ml}$  in 15 cm-deep overlying water.

Phosphorus adsorption maxima were determined to evaluate the capacity of wetland soils to retain phosphorus. The estimated adsorption maxima for the soils investigated ranged from 62 to 2,030  $\mu\text{g P/g}$  soil. The results showed that soils in the retention/detention area have high phosphorus removal potential as indicated by significantly

higher values for adsorption maxima than the amount of native phosphorus in the soils.

The effect of aerobic and anaerobic conditions on phosphorus retention was also studied. Adsorption characteristics were influenced by aerobic and anaerobic soil conditions; however, considerable amounts of phosphorus were shown to be retained by most soils (except Myakka soil) under either condition. In most cases, phosphorus was apparently retained through an organic matter-Al- $\text{PO}_4^{-3}$  bridge. For soil with very high calcium content, such as the Placid soil, Ca- $\text{PO}_4^{-3}$  interaction was very likely responsible for phosphorus retention. In soils with high iron content, iron seemed to play an important role in phosphorus retention under anaerobic conditions. When soils became anaerobic, ferric iron was reduced to ferrous iron which can precipitate with phosphate at high solution phosphorus concentrations.

In a simulated wetland system, underlying soil was observed to adsorb phosphorus readily from the overlying water. By 25 days, approximately 54 to 88% of the initial overlying water phosphorus was removed. The phosphorus removal rates during the investigation period ranged from 0.05 to 0.08  $\mu\text{g P/ml/day}$ . These values are equivalent to the phosphorus removal rate of 75-120 g P/ha/day, assuming a depth of overlying water of 15 cm. Therefore, more phosphorus can be removed by soil with increasing residence time of the overlying water. There also has been a study showing that phosphorus sorption sites in soils can be regenerated with time, especially after drying and wetting cycles (Sawhney and Hill, 1975).

Soil in wetland retention/detention areas can also affect nutrient availability from plant materials decaying at the water-soil interface.



The rate of plant decomposition in wetland ecosystems decreased with decreasing pH. In these laboratory systems, the pH was controlled largely by the pH of the underlying soil. This would also likely be the situation in many wetland systems with relatively slow water flow. In systems with a greater water flow, the pH of the soil in the surrounding watershed would likely have a greater influence. Aeration did not have a measurable effect on rate of plant decomposition.

Inorganic nitrogen release to the overlying water was apparently limited by the high C:N ratio of the decomposing plant material which resulted in most of the original plant nitrogen being recycled in microbial biomass. Although about 50% of the original phosphorus in the plant material was released, two of the soil systems had the capacity to adsorb nearly all of the released phosphorus with essentially no release into the overlying water. The third soil, having a lower adsorption maximum than the other two soils, was not able to remove all of the released phosphorus. Calcium and potassium released from the decaying plant material were retained in small amounts by the soils but most remained in the overlying water during the 16 week incubation period.

A general conclusion of this research is that wetland soil can effectively remove nitrogen and phosphorus from agricultural drainage water. Nitrification/denitrification reactions may be responsible for a significant amount of nitrogen loss. Overlying water nitrate removal rates can be influenced by soil pH and amount of available carbon. A relatively small amount of nitrate was reduced to ammonium and immobilized into organic nitrogen. Phosphorus from the overlying water

was essentially removed by adsorption to soil. Considerable amounts of phosphorus can be readily adsorbed to soil under either anaerobic or aerobic conditions. Phosphorus retention by soil was shown to be dependent on soil characteristics such as organic matter content, iron, aluminum and calcium contents. Furthermore, wetland soil can affect the rate of plant material decomposition and associated nutrient release. This research also suggests that nutrient release to overlying water cannot be predicted by the extent of vegetation decomposition alone and that interactions between the released nutrients and soils can have a significant effect on the final fate of the nutrients.

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## BIOGRAPHICAL SKETCH


Duangporn Sompongse was born in Bangkok, Thailand, on February 9, 1954, the first of four children of Mr. and Mrs. Chaon Sompongse. She had her early education at Strividhya School in Bangkok. In May 1970, she came to Ft. Pierce, Florida, to stay with her uncle and aunt, Mr. and Mrs. T.R. Robinson. She attended Ft. Pierce Central High School for 2 years and graduated in June 1972. Then she began her college career at Indian River Community College, and received an Associate of Arts degree with highest honors in August 1973. She transferred to the University of Florida in September 1973 and received a Bachelor of Science degree in chemistry with honors in June 1975. In September 1975, she started her graduate study in the Department of Environmental Engineering Sciences and received a Master of Science degree in August 1978.

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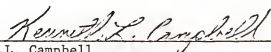
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